PB-227 420

ADVANCE WASTE TREATMENT AND WATER REUSE SYMPOSIUM HELD AT ADOLPHUS HOTEL, DALLAS, TEXAS ON JANUARY 12-14, 1971. SESSION 2

Ladd S. Davies, et al

Federal Water Quality Administration
Cincinnati, Ohio

1971

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

PB 227 420

ADVANCE WASTE TREATMENT AND
WATER REUSE SYMPOSIUM

Adolphus Hotel
Dallas, Texas
January 12-14, 1971

Sponsored By

Environmental Protection Agency

Co-sponsored By

Arkansas Pollution Control Commission
Louisiana Stream Control Commission
New Mexico Health and Social Services Department
Oklahoma Pollution Control Coordinating Board
Texas Water Quality Board

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151

Session #2

Moderator:	Ladd S. Davies, Director Arkansas Pollution Control Commission
1:45 P.M.	Measurement & Forms Of Nitrogen & Phosphorus Edwin F. Barth
2:15 P.M.	Oxygen Aeration For Secondary Treatment Richard C. Brenner
2:45 P.M.	Coffee Break
3:00 P.M.	Biological Nitrification & Denitrification Edwin F. Barth
3:45 P.M.	Ammonia Removal: Specific Ion Exchange & Air Stripping Dr. Joseph B. Farrell
4:30 P.M.	Summary Ladd S. Davies

CONTENT

Measurement And Forms Of Nitrogen And Phosphorus
Edwin F. Barth

Oxygen Aeration For Secondary Treatment
Richard C. Brenner

Nitrogen Removal From Wastewater
Advanced Waste Treatment Research Laboratory
Cincinnati, Ohio

ADVANCED WASTE TREATMENT AND

WATER REUSE SYMPOSIUM

January 12-14, 1971

Dallas, Texas

Contents:

MEASUREMENT AND FORMS OF NITROGEN AND PHOSPHORUS

Edwin F. Barth
Advanced Waste Treatment Research Laboratory
U.S. Department of the Interior
Federal Water Quality Administration
Ohio Basin Region
Cincinnati, Ohio

MEASUREMENT AND FORMS OF NITROGEN AND PHOSPHORUS

As our wastewater treatment goals increase in scope it becomes critical that good analytical control of processes be employed.

In order to implement and control nutrient removal processes we need a basic understanding of the chemistry of the elements nitrogen and phosphorus.

Phosphorus and nitrogen have many similar chemical reactions but there are some important dissimilarities.

A major difference between compounds of these two elements is that most of the phosphorus compounds we deal with in wastewater treatment are insoluble, while most of the nitrogen compounds are soluble.

In biological processes phosphorus is a conservative element. Loss to the atmosphere is not probable. In environmental situations phosphorus cycles between organic and inorganic forms. Microenvironments can have a great effect on availability of phosphorus.

The phosphorus procedure given in Standard Methods is for boiler water analysis and will not measure all forms of phosphorus present in wastewater. To measure treatment efficiency a total phosphorus procedure is necessary. Coupled with the total phosphorus assay it can be useful to filter a sample to determine the influence of liquid-solid separation processes.

Careful control of the final colorimetric assay conditions is important for accurate values and to avoid interferences.

With the increased interest in nitrogen in the environment the analysis for the various forms of nitrogen are assuming increased importance. The methods for organic nitrogen, ammonia nitrogen, nitrite, and nitrate are specific for each form. To completely account for nitrogen in a treatment system all these forms must be measured.

Preservation of samples is an important consideration in order to insure that loss or transformation to another species does not occur. Rapid freezing of samples for preservation is the most suitable method.

Automated methods are needed to collect sufficient data for evaluation. Careful attention is needed to insure that the electronic signal recorded is representative of the specific component desired.

The attached tables and figures will be used to present this topic.

TABLE 1

WASTEWATER TREATMENT GOALS

1900-1920 HISTORIC

REMOVE SUSPENDED SOLIDS
REMOVE OXYGEN DEMANDING MATERIALS
TRANSFORM NH_4^+ TO NO_3^-

1920-1964 CONTEMPORY

REMOVE SUSPENDED SOLIDS
REMOVE BOD_5
PROTECT RECEIVING WATER FROM TOXICANTS
CONTROL COLIFORMS

1964-CURRENT TREND

REMOVE SUSPENDED SOLIDS
REMOVE OXYGEN DEMANDING MATERIALS
REMOVE PHOSPHORUS
TRANSFORM NH_4^+ TO NO_3^- OR REMOVE NITROGEN
PROTECT RECEIVING WATER FROM TOXICANTS
CONTROL COLIFORMS
POSITIVE CONTROL OF SLUDGES AND BRINES

Element	Symbol	Valences	Usual form
Nitrogen	N	3, 5, 1, 2, 4	Gas
Phosphorus	P	3, 5, 1, 4	Waxy solid
Arsenic	As	3, 5	Metallic solid

Compounds with similar properties

HNO_3	N_2O_3	NCl_3	NH_3
H_3PO_4	P_2O_3	PCl_3	PH_3
H_3AsO_4	As_2O_3	$AsCl_3$	AsH_3
↑ Acid strength	↑ Reactivity	↑ Unstable nature	↑ Stable nature

Similar compounds with different properties

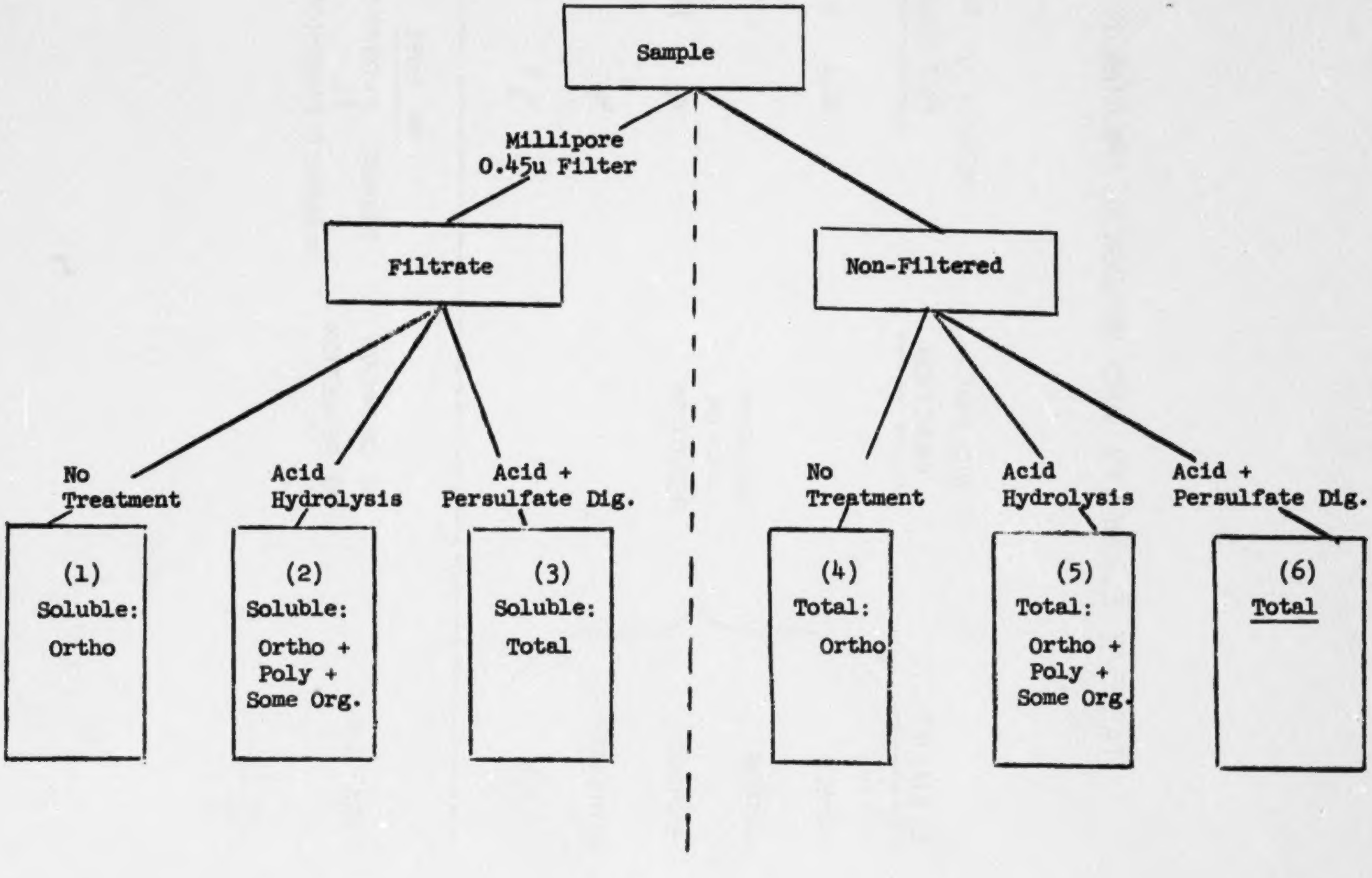
Soluble: $Ca(NO_3)_2$ $Al(NO_3)_3$ $Fe(NO_3)_3$

Insoluble: $Ca_3(PO_4)_2$ $AlPO_4$ $FePO_4$ $(NH_4)MgPO_4$

TABLE II. ELEMENTS AND BIOLOGICAL TREATMENT

ELEMENT	BIOLOGICAL REACTION	RESULT OF TREATMENT NET LOSS
OXYGEN	OXIDATION AND/OR REDUCTION	CO_2 CH_4
CARBON		
HYDROGEN		H_2 H_2O
NITROGEN		N_2
SULFUR		H_2S
		NO LOSS
PHOSPHORUS	NO OXIDATION NO REDUCTION	ORGANIC PHOSPHORUS $\uparrow\downarrow$ INORGANIC PHOSPHORUS

Determination of Various Phosphorus Forms


Sample
Millipore
0.45u Filter
Filtrate
Non-Filtered
No
Treatment
Acid
Hydrolysis
Acid +
Persulfate Dig.
(1)
Soluble:
Ortho
(2)
Soluble:
Ortho +
Poly +
Some Org.
(3)
Soluble:
Total
No
Treatment
Acid
Hydrolysis
Acid +
Persulfate Dig.
(4)
Total:
Ortho
(5)
Total:
Ortho +
Poly +
Some Org.
(6)
Total

Data Treatment	Phosphorus Components Determined
	A. Soluble Forms
1	1) ortho
2	2) ortho + poly + some org's.
3	3) total
2 - 1	4) poly + some org's.
3 - 2	5) most org's.
	B. Total Forms
4	6) ortho
5	7) ortho + poly + some org's.
6	8) total
5 - 4	9) poly + some org's.
6 - 5	10) most org's.
	C. Particulate Forms
4 - 1	11) ortho
(5-4) - (2-1)	12) poly + some org's.
(6-5) - (3-2)	13) most org's.
6 - 3	14) total

Forms and Measurements of Phosphorus

Phosphoric Anhydride	P_4O_{10} (usually calculated as P_2O_5)

Orthophosphates Found in Water

Phosphoric acid	H_3PO_4 below pH 2.2
Dihydrogen phosphate ion (monovalent)	$H_2PO_4^-$ from pH 2.2 to 7.2
Monohydrogen phosphate ion (divalent)	$HPO_4^{=}$ from pH 7.2 to 12.4
Phosphate ion (trivalent)	$PO_4^{\equiv}$ above pH 12.4
Dicalcium phosphate	$CaHPO_4$ from pH 6 to 8

(Tricalcium phosphate, $Ca_3(PO_4)_2$, does not form in water)

Hydroxyapatite	$Ca_5OH(PO_4)_3$ above pH 7-8
Fluorapatite	$Ca_5F(PO_4)_3$ above pH 7

Aluminum hydroxide adsorbs $HPO_4^{=}$ from pH 5 to 10

Aluminate ion $Al(OH)_4^-$ forms above pH 10

Ferric hydroxide adsorbs $HPO_4^{=}$ above pH 4

Magnesium hydroxide flocculates colloidal phosphates above pH 10-11

Polyphosphates

All polyphosphates hydrolyze slowly to orthophosphates

Sodium Trimetaphosphate	$Na_3(PO_3)_3$ -- a ring compound
Sodium Polymetaphosphate	$(NaPO_3)_n$ -- a long chain

(there is no justification for the name "hexametaphosphate")

Sodium Pyrophosphate	$Na_4P_2O_7$
Sodium Tri Polyphosphate	$Na_5P_3O_{10}$

Organic Phosphates

Esters and anhydrides	$ROPO_3^{=}$, $ROPO_3PO_3^{=}$
Phosphagens	$RNPO_3^{=}$

Reference

(1) Van Wazer, J. R. Phosphorus and Its Compounds. Interscience 1958.

PHOSPHORUS COMPOUNDS CLASSIFIED BY CHEMICAL AND SOLUBILITY RELATIONS(1)

Form	Water Soluble(2)	Insoluble(2)
1. Ortho phosphates $(PO_4)^{-3}$	Combined with monovalent cations such as H, Na, K, NH_4	Combined with multi valent cations such as $CA^{+2}Al^{+3}Fe^{+3}$
2. Poly phosphates $(P_2O_7)^{-4}$, $(P_3O_{10})^{-5}$ $(P_3O_9)^{-3}$ and others depending upon the degree of dehydration.	(a) as in 1 (above), but solubility decreases as molecular weight increases	(a) as in 1 (above) (b) multi P polyphosphates (high mol. wt.) including the "glassy" phosphates
3. Organic phosphorus R-P, R-P-R (3) (unusually varied nature)	(a) certain chemicals (b) degradation products (c) enzyme P (d) phosphorylated nutrients	(a) certain chemicals (b) cell mass, may be colloidal or agglomerated (c) soluble P sorbed by insoluble residues
4. Mineral phosphorus	(a) as in 1 (above), but solubility decreases for complex forms	(a) as in 1 (above) (b) geological P such as phosphosilicates (c) certain mineral complexes

---

(1) Table drawn from a lecture, "Determination of Phosphorus in the Aqueous Environment," by F. Ludzack, FWPCA Training Activities, Ohio Basin Region.

(2) Used to indicate usual state under common conditions.

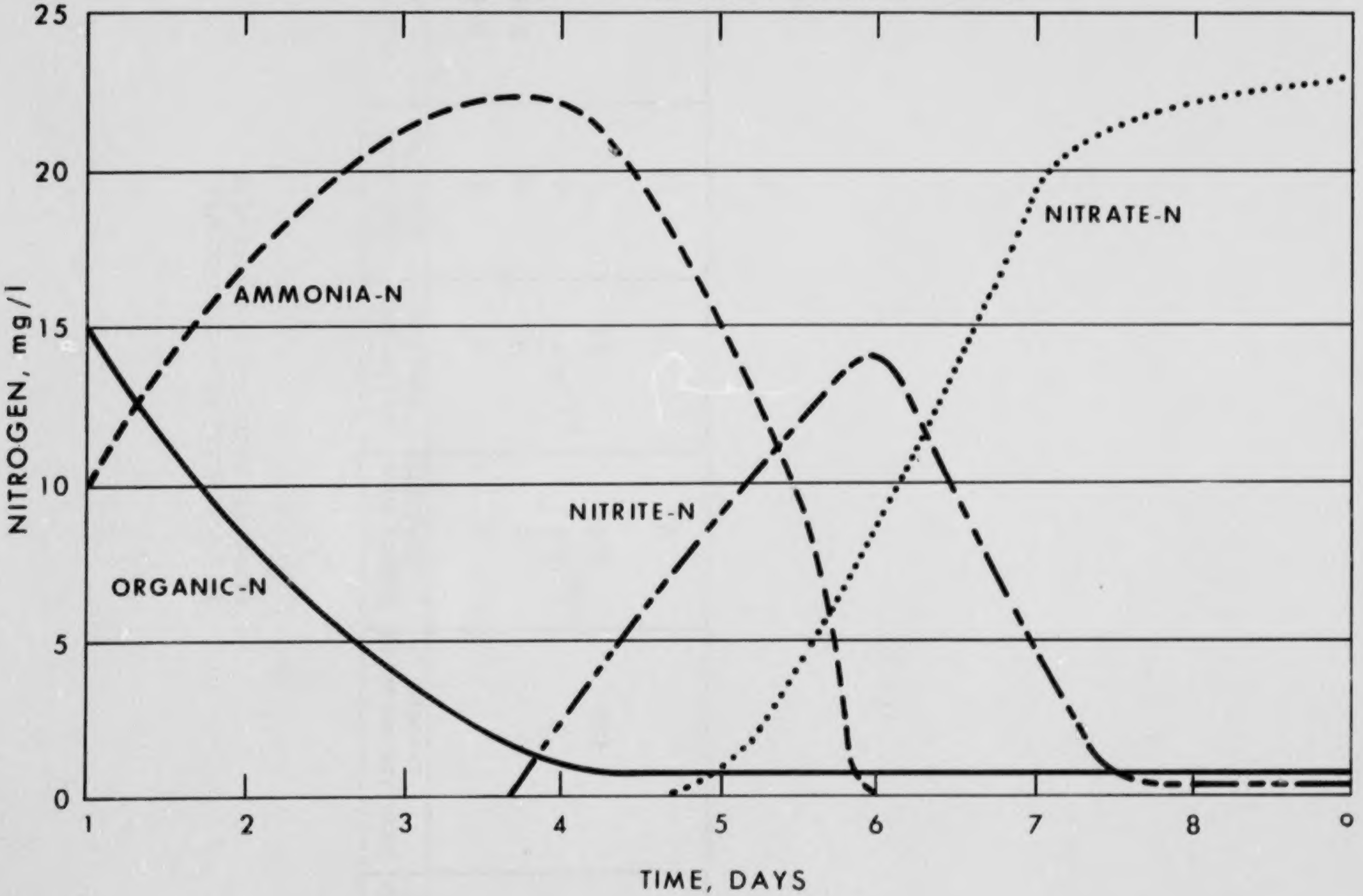
(3) R represents an organic radical, P represents P, PO_4, or its derivatives.

Effect of Varing Sulfuric Acid - Ammonium Molybdate Ratio on Heteropoly Blue Color Development
(Stannous chloride in glycerine reductant)

Acid Molybdate Reagent Composition		Normality* of acid in final 100 ml assay volume	Absorbancy (O.D.)	
Ammonium Molybdate gm/100 ml	Concentrated Sulfuric Acid ml/100 ml		Distilled Water	0.05 mg P Standard
2.0	5	0.072	> 2.0	> 2.0
2.0	10	0.144	0.805	1.00
2.0	15	0.216	0.260	0.580
2.0	20	0.288	0.036	0.475
2.0	25	0.360	0.004	0.415
2.0	30	0.432	0.000	0.365
2.0	35	0.504	0.000	0.345
2.0	40	0.576	0.000	0.252
2.0	50	0.720	0.000	0.060
2.0	60	0.864	0.000	0.012

*Calculated normality of H_2SO_4 in the 100 ml final volume produced by using 4.0 ml of the particular acid molybdate solution.

NITROGEN TRANSFORMATIONS



Nitrogen Forms in 1:1 Mixture of High-Rate and Nitrified Effluents

Nitrogen Form	High-Rate Effluent	Nitrified Effluent	Denitrified Effluent	Oxidized Nitrogen Removal	Over-All Removal
Organic-N	5	2	3		
Ammonia-N	10	0	5		
NO_2-N	-	1 > 13	0.5 > 1.0		
NO_3-N	-	12	0.5	92%	
Sum	15	15	9		40%

VAN SLYKE REACTION

$$\mathrm{RNH_2 + NO_2^- \xrightarrow{acid} ROH + N_2\uparrow + H_2O}$$

ADVANCED WASTE TREATMENT AND

WATER REUSE SYMPOSIUM

January 12-14, 1971

Dallas, Texas

p. 3

HIGH PERCENTAGE OXYGEN AERATION
FOR SECONDARY TREATMENT

p. 52

Richard C. Brenner
Advanced Waste Treatment Research Laboratory
U.S. Department of the Interior
Federal Water Quality Administration
Ohio Basin Region
Cincinnati, Ohio

HIGH PERCENTAGE OXYGEN AERATION FOR SECONDARY TREATMENT

Richard C. Brenner

INTRODUCTION

The concept of using oxygen enriched air or pure oxygen as the aeration gas in the activated sludge process has intrigued investigators for over twenty years. In 1948, Pirnie (1) suggested a method of predissolving oxygen in wastewater prior to activated sludge treatment. The following year, Okun expanded on Pirnie's model and developed his "bio-precipitation system" which utilized an integral upflow bio-reactor and clarifier (2). Later, Budd and Lambeth (3) evaluated Okun's "bio-precipitation system" in a large pilot plant and reported an oxygen absorption efficiency of 20-25% with power requirements equal to the conventional diffused air technique.

The inherent characteristic of oxygen gas which has created so much interest over the years is its high partial pressure. At atmospheric pressure, the partial pressure of pure oxygen gas is 760 mm of mercury while the partial pressure of oxygen in air is only 160 mm of mercury. Thus, the driving force for dissolving oxygen in water is 4.75 times higher with pure oxygen.

In a "state-of-the-art" review, McKinney and Pfeffer (4) concluded that if the potential of high percentage oxygen aeration could be harnessed in an economically realistic fashion, the following benefits to the activated sludge process could conceivably be achieved:

1. Reduction of power required per unit of oxygen transferred.
2. Reduction in, or elimination of, periods of zero dissolved oxygen concentration.
3. Increased rate of stabilization of organic material.
4. Ability to operate high rate systems with substantial increases in organic loading where oxygen is not limiting.
5. Increased capacity of organically overloaded plants without need for additional aerator capacity.
6. Reduction in plant size and capital investment.

Until recently, however, serious consideration of oxygen aeration has not progressed past the laboratory and pilot plant stages. The basic problem has been the lack of an effective oxygen gas contacting system with a built-in high overall utilization factor. Since oxygen is an expensive commodity and since conventional aeration techniques would vent the major fraction of the input oxygen to the atmosphere, the widespread impression has been that oxygen aeration must, of necessity, be significantly more costly than air aeration. This rationale led Okun and Lynn (5) to conclude in 1956 that the substitution of oxygen for air or the use of oxygen enriched air in standard activated sludge aeration tanks would not be economically feasible because of the poor oxygen transfer efficiency inherent in diffuser and tank design.

Okun and Lynn's position as stated above has proven to date to be partially correct. Certainly, the requirements for an economical oxygen contacting system are such that conventional air aeration technology is entirely inadequate. However, what Okun and Lynn did not forsee was the covering of standard activated sludge tanks to form a gas tight structure. An efficient oxygen aeration system (which will be discussed at length in the following sections) has been developed which utilizes covered longitudinal aeration tanks. The development of an efficient open tank oxygen aeration system also appears to be within the realm of feasibility.

STIMULATION OF RENEWED INTEREST IN OXYGEN AERATION

In early 1968, the Linde Division of Union Carbide approached the FWQA concerning a new oxygen gas contacting concept developed in their laboratories. According to Union Carbide, this concept satisfied all the basic requirements of a cost effective oxygen dissolution system:

1. High percentage oxygen absorption and utilization (i.e. >90%).
2. High overall energy transfer efficiency as compared with air aeration systems.
3. Efficient liquid mixing sufficient to maintain uniform mixed liquor composition.
4. Simple design with low maintenance costs.
5. Low capital investment.

Continuing discussions culminated in the awarding of a $528,000 FWQA Research and Development Contract to Union Carbide in October, 1968. The contract was carried out at the Batavia, New York Treatment Plant. Under the terms of the contract, the performance and economics of the

Linde oxygen aeration (oxygenation) system were evaluated and compared with those of a parallel air aeration system from May to November of 1969.

CONFIGURATION AND OPERATION OF OXYGENATION SYSTEM

A schematic respresentation of the Union Carbide oxygenation system is shown in Figure 1. A gas tight cover on top of the aeration tank is utilized to prevent oxygen leakage to the atmosphere. Baffles are installed to form a series of staged comartments down the length of the aerator. Each compartment is equipped with a submerged turbine-rotating sparger combination. A recirculating gas compressor is located on top of or adjacent to each compartment.

Liquid waste and oxygen gas flow are cocurrent with both being introduced to the head of the aeration tank. Recycle sludge also enters at this point. Oxygen gas fed to the first compartment is compressed and forced down the hollow shaft of the submerged turbine and out through the rotating sparger. The fine bubbles thus created are dissolved in the mixed liquor. The propeller blades furnish bulk fluid mixing and create a downward pumping action which provides longer residence time for the bubbles.

Oxygen which is not utilized by microorganisms vents back into the head space of the first compartment. Here it is either compressed and recirculated again or, due to the slight positive pressure of 1-3" water column maintained in the gas phase, moves through an appropriately sized opening in the baffle wall to be used in the second compartment by the same technique. In like fashion, vent gas from each compartment is used in the succeeding compartment until the end of the aeration tank is reached. A small exhaust stream (10-20% of the input gas stream) vents to the atmosphere from the last compartment. It should be pointed out that the gas stream is picking up reaction products and inert gases as it proceeds down the compartments. The exhaust gas is, therefore, about 50% oxygen, and 50% carbon dioxide, nitrogen, argon, etc. The small exhaust rate and the reduced composition of oxygen in the exhaust gas combine to yield an overall oxygen utilization of 90-95%.

SCOPE OF THE BATAVIA PROJECT

The nominal capacity of the Batavia plant is 2.5 mgd. As indicated in Figure 2, the plant consists of two parallel and identical 1.25 mgd aeration tanks each with its own final clarifier and separate return sludge line. Each aeration tank has two passes. There are no primary settlers at Batavia. Raw wastewater is screened, degritted, and comminuted before entering the aerators. Waste activated sludge is handled in sequence by gravity thickening, two stage anaerobic digestion, vacuum filtration, and trucking to disposal. Treated effluent is chlorinated before discharge to Tonawanda Creek.

The oxygenation system was installed in one of the two aeration tanks. A temporary steel deck cover was bolted and sealed to the top of the oxygen aerator for convenience and economy. Baffle installations were also designed for short term use. Six compartments or stages were utilized, three in each pass. Oxygen was stored on site in the liquid form and then vaporized before introduction to the oxygen aerator. Oxygen feed rate to the first compartment was automatically controlled by maintaining a constant vapor pressure in the gas space of 1-3" of water. Dissolved oxygen level was also automatically controlled, but in the first compartment only where oxygen demand was highest. This was accomplished with a dissolved oxygen probe and a feedback signal which controlled the rate of recirculation of the first stage compressor.

The existing diffused air system was left intact in the second aerator for the comparative studies. Aeration capacity of this train was increased with 50% additional laterals and diffusers. Compressed air was supplied to the air train by the plant's rotary blowers.

The experimental program was segmented into three phases; a conservative phase, a medium stressed phase, and a highly stressed phase. To take advantage of dry weather flow, the highly stresed phase (Phase II) was conducted in the summer immediately after the conservative phase (Phase I). The medium stressed phase (Phase III) was conducted last. The modes of operation of the three phases are given in Figures 3, 4, and 5.

In Phase I, the average plant flow of 3.88 mgd was divided evenly as nearly as possible between the two trains. All six compartments of the oxygen train and both passes of the air train were utilized. The intended aeration detention time in each train based on raw flow was 6 hours, but the high spring flows reduced this to about 4 hours. Seven weeks of comparative data were collected in this phase.

All of the plant flow was directed to the oxygen train in Phase II. To further stress the system, three of the six stages were taken out of service. Both clarifiers and air lift pumps were utilized to separate and return the sludge. The intended and actual aeration time averaged 1.5 hours. Seven weeks of data were also collected in this phase.

The plant flow was again split between the two trains in Phase III. Three of the six oxygen compartments and one pass of the air train were taken out of service to achieve a medium loaded condition. The intended aeration detention time of 3 hours was realized with the air train. The detention time of the oxygen train averaged somewhat lower at 2.8 hours. Nine weeks of comparative data were collected in this phase.

SUMMARY AND DISCUSSION OF BATAVIA PERFORMANCE DATA

Comparative performance data generated on the Batavia project are summarized in Figures 6 through 9. Each of the data figures will be discussed in order below:

Figure 6: Excellent operation and surveillance were given to both systems throughout. The degree of operator attention was 2-3 times that normally expended at treatment plants. Well-trained Union Carbide technicians operated the experimental facilities during the week; Batavia plant personnel were utilized on the weekends.

It was decided to operate the air train in Phase I at a mixed liquor suspended solids (MLSS) concentration typical of other conventional air systems of approximately 2500 mg/l. MLSS in the oxygen train in Phase I were kept at 40-50% of the maximum concentration which it was anticipated could be carried in later phases, or about 3000 mg/l. In order to treat effectively under the high rate loading conditions of Phase II, oxygen train MLSS were raised to the maximum sustainable level of 7000 mg/l. This upper limit was not due to oxygen transfer limitations but to restricted clarification capacity. In Phase III, oxygen train MLSS were kept high at about 6200 mg/l while air train MLSS were raised to the maximum point (3700 mg/l) at which some measurable dissolved oxygen (DO) could still be maintained in the mixed liquor. Above 3700 mg/l, DO fell to zero and septic odors commenced.

Sludge settled very well in both systems. Sludge volume index (SVI) varied from 35-65 for the oxygen system and 65-75 for the air system. In both systems, SVI decreased with increasing MLSS. In all probability, the extremely good settling characteristics were due in part to the absence of primary sedimentation.

Recycle sludge concentration was also higher than in most plants. For the air system, the concentration ranged from 1.5-1.6%. The range for the oxygen system was 1.8-3.0%. Recycle sludge concentrations in the oxygen system as high as 4% were noted in Phase II during the day. The installation of a larger flow meter in the oxygen train sludge recycle line to handle the return from both clarifiers in Phase II adversely affected oxygen slydge recycle concentration in Phase III. Return flow had to be kept artificially high in Phase III to maintain sufficient head loss to operate the oxygen air lift pump, thereby thinning out the sludge. It is felt that with more conservative overflow rates and variable speed return pumps, oxygenated sludge can be thickened routinely to 3-4% in the final clarifier. At these concentrations, it is doubtful if the waste oxygenated sludge would have to undergo separate thickening before digestion or direct vacuum filtration.

Mixed liquor DO averaged 8-9 mg/l in the oxygen train in all phases. Variations in DO profile down the stages were insignificant. The low oxygen effluent DO in Phase II indicates that some treatment was still going on in the final clarifier due to the high organic loading. Air train mixed liquor DO was low in both Phases I and III. No measurable DO was present at the head of the air aerator in either phase, despite abnormally high system air input rates of 3-4 ft^3/gal of sewage treated. The poor oxygen transfer efficiency of disc diffusers is readily apparent.

Figure 7: As anticipated, BOD and suspended solids (SS) removals were good for both systems in the conservative Phase I. Effluent COD values of 73 mg/l for the oxygen train and 84 mg/l for the air train are considered acceptable for aerators treating unsettled sewage. Volumetric organic loadings were in the upper portion of the range for which most conventional plants are designed. Overall performance in Phase I was slightly better for the oxygen train.

One of the most encouraging aspects of the entire project was the acceptable level of performance of the oxygen system under the high rate conditions of Phase II. Effluent BOD, COD, and SS values were not as low as in Phase I but still within the range of good secondary treatment. The volumetric organic loading was 3-1/2 times higher than in Phase I. The ability of the oxygen system to operate satisfactorily under much higher organic loading rates than normally associated with air systems was clearly established in this phase.

Wastewater feed strength was at its highest in Phase III. Some problems were encountered with the flow splitting device to the two aerators with the result that about 10% more flow was directed to the oxygen train. Performance of the oxygen train was excellent. Percent removals of BOD, COD, and SS were the highest of any of the three phases although absolute effluent concentrations were slightly higher than in Phase I. The air system began to show signs of performance deterioriation in Phase III. There was zero DO in the air train effluent. Effluent BOD and SS concentrations were about double and effluent COD 30% higher than those of the oxygen system. Volumetric organic loadings were more than twice as high as in Phase I.

Somewhat unexpected was the magnitude of the reduced quantities of waste activated sludge generated throughout the study in the oxygen system. Disregarding the data point for the oxygenation system in Phase III (which is extremely out of balance with the other two phases), 30-40% less sludge was wasted from the oxygen system than from the air system. Considering that sludge handling and disposal account for 1/2 to 2/3 of total annual treatment costs, this factor assumes significant economic importance. From the above data, it is evident that oxygenation is a highly oxidative process.

Figure 8: The two principal conclusions which can be drawn from these data are that phosphorus removal was in the range normally associated with biological uptake for both systems and that neither system nitrified. For the two comparative phases, phosphorus removal averaged 5% higher for the air system. This is to be expected as the oxygen system "burned up" more sludge and thereby, in all likelihood, solubilized greater quantities of stored cellular phosphorus. Only the very beginnings of incipient nitrification were noticed in either unit. This was the one disappointing feature of the Batavia oxygen train performance, notwithstanding that prevailing temperatures and organic loading rates were not exactly conducive to nitrification.

Figure 9: High percentage utilization of feed oxygen was achieved at greater than 90% in each phase. The average composition of oxygen in the exhaust gas for the project was 51%.

Power consumption for oxygen dissolution is broken into two categories, liquid mixing and gas recirculation. Power consumption for liquid mixing is roughly proportional to the gallons of mixed liquor under oxygenation while gas recirculation power is highly dependent on waste strength and the total pounds of BOD or COD entering the system. It should be pointed out that the oxygen compressors used on this project were substantially oversized for experimental flexibility and that the power requirements shown here for gas recirculation represent only that fraction of gas which was actually put through the turbine shaft. Power consumed in bypassing unneeded gas is not included. This is a legitimate technique as in a non-experimental situation, compressors are sized more closely to design conditions and variable speed compressors are used in the high oxygen demand stages.

Abnormally high aeration rates were required in the air train in an attempt to cope with the high organic strength of the unsettled wastes. This resulted in an air blower power requirement of 5-6 times that for oxygen dissolution. For a true comparison of total power requirements, however, the power consumed in on-site oxygen gas production should be added to that used in oxygen dissolution. Since liquid oxygen was used in this project, no such totals are possible here. In general, though, power requirements for oxygen generation will range from 1.3 to 1.7 times greater than the power required for oxygen dissolution. Even so, a considerable reduction in overall power costs with oxygen is indicated..

ECONOMIC PROJECTIONS

The following assumptions are used in conjunction with the Batavia data in arriving at comparative cost curves for the two systems:

1. Raw sewage pumping and metering, preliminary treatment (including screening, comminution, and grit removal), primary sedimentation, service and administration buildings, and outside piping and appurtenances are costed in equally for both systems.

2. Raw wastewater BOD is assumed to be 200 mg/l with 35% removed in the primary settlers.

3. Equal amounts of primary sludge are produced in each system at the rate of 860 lb/mil gal treated. Waste activated sludge quantities for the two systems are in accordance with Figure 10 which was derived from the Batavia data. Phase III oxygen system waste sludge data were not used in constructing Figure 10.

4. MLSS concentration for the oxygen and diffused air systems are assumed to be 6800 mg/l and 2500 mg/l, respectively, with 65% of the sludge being volatile in each case.

5. Based on assumption 4 and using Figure 11 which was compiled from the Batavia work, 1 hour of oxygen aeration will provide equivalent treatment to 3 hours of air aeration.

6. For each size plant costed, four aeration detention points (based on raw flow) are plotted and compared. These points are 1.0, 1.33, 1.66, and 2.0 hours for oxygen and 3.0, 4.0, 5.0, and 6.0 hours for air. Percent BOD removal associated with each set of comparative points is given in Figure 12. Volumetric organic loadings and food to biomass ratios for the various aeration detention times are shown in Figure 13.

7. Due to the variance in oxygen transfer capability of different types of air diffusers, three air aeration rates are costed for the air system including 0.8, 1.6, and 2.4 ft^3/gal wastewater treated.

8. Oxygen supply varies from 1.0 to 1.22 lb/lb BOD removed as oxygenation detention time increases from 1.0 to 2.0 hours. Average oxygen utilization is 91%.

9. Mixed liquor DO is assumed at 8 mg/l for the oxygen system and 1 mg/l for the air system.

10. Sludge recycle oncentrations are assumed to be 40,000 mg/l and 10,000 mg/l, respectively, for oxygen and air systems.

On these bases, average sludge recycle rates in the same order are 20% and 33% of influent flow. Spare recycle pump capacity of 100% average recycle flow is costed in for each system.

11. Oxygen is supplied to the oxygenation system by on-site generation of oxygen gas. For plant sizes up to approximately 30 mgd, the generation plant would be of the air separation type. Above 30 mgd, a cryogenic plant is used. Union Carbide has made a managerial decision that municipalities, if they so choose, may purchase the plant outright rather than purchasing liquid or gaseous oxygen across the fence. The savings to the municipality in $/ton of oxygen by buying the plant instead of the commodity itself are evident in Figure 14. The bottom curve is used in the cost projections given herein.

12. Total oxygenation system and air aeration system power requirements for the four plant sizes (1, 6, 30, and 100 mgd) used later in the comparative cost curves are indicated in Figures 15 and 16, respectively. Power requirements for the oxygen system are a function of oxygenation detention time; those for the air system are a function of air aeration rate. Reserve air system blower capacity of 100-25% is provided as plant size increases from 1 to 100 mgd. Backup capacity for the oxygen generators includes a spare air compression unit for the 1, 6, and 30 mgd plant sizes and a 24-hour on-site supply of liquid oxygen for the 100 mgd plant.

13. Sludge disposal for the 1 mgd plant is assumed to be by anaerobic digestion followed by sludge drying beds, for the 6 mgd plant by anaerobic digestion, vacuum filtration, and cake disposal by land fill, and for the 30 and 100 mgd plants by anaerobic digestion, vacuum filtration, and incineration. Both primary and waste activated sludges were costed into the sludge disposal estimates.

14. A gravity thickener is costed in for the air system to thicken waste activated sludge from 1 to 4% prior to anaerobic digestion. Since it is assumed that waste activated sludge is drawn from the oxygen system at 4%, a thickener is not needed for the oxygen system.

15. Secondary clarifiers are sized at 800 gal/day/ft^2 for both systems at a liquid depth of 10 ft for the air system and 11 ft for the oxygen system.

16. Cost curves and formulae for construction and operation of conventional plant units and for sludge thickening and disposal were supplied to Union Carbide by FWQA. Cost data for oxygen generation, dissolution, and control equipment and for oxygenation tank covers and baffles were furnished by Union Carbide. Amortization was calculated at 5-1/2% over 25 years. Construction costs were determined using January, 1970 indices.

The above assumptions have been compiled into four comaparative cost estimate curves for 1, 6, 30, and 100 mgd plant sizes. These cost estimates are given in Figures 17 through 20 as total treatment costs in ¢/thousand gallons treated. The costs reflect debt retirement and operation and maintenance of all plant facilities including sludge disposal equipment, i.e. the total cost associated with running a combined primary-secondary treatment plant with the exception of effluent chlorination.

As can be seen in Figure 17, there is no cost advantage with oxygen at 1 mgd. At the 6 mgd scale, there is an estimated cost savings with oxygen ranging from 11-15% when compared with an air aeration rate of 0.8 ft^3/gal and 17-21% when compared with an air aeration rate of 1.6 ft^3/gal. For the 30 mgd plant, estimated cost reductions with oxygen range from 16-20% and 21-27% for the comparisons with 0.8 and 1.6 ft^3/gal, respectively. At 100 mgd, the estimated cost reductions with oxygen are 17-25% and 22-29% compared to the same air aeration rates, respectively.

It is emphasized that the cost data shown in these figures are estimates only and that individual plant costs may vary widely with locale. Further, it is realized that air aeration equipment vendors, particularly those that manufacture surface and turbine aerators, may disagree with the air system design used in the cost comparisons. Nevertheless, it is believed the air system design so presented reflects conventional plug flow designs as they are approved by state regulatory agencies and used in the majority of the municipalities in this country. Likewise, the oxygen system design presented herein reflects the manner in which it is contemplated such a system would be designed for a municipal installation.

APPLICATIONS OF THE OXYGEN AERATION PROCESS

It is felt the results of the Batavia project justify consideration of the oxygen aeration process for all new secondary plants and primary plants expanding to secondary treatment. In this type of application, the City of Detroit, Michigan has solicited bids with State of Michigan and FWQA Construction Grants approval for a 300 mgd oxygen aeration module for its new METRO plant. Also, the State of New York has approved plans for a 15 mgd oxygen aeration system at New Rochelle, New York.

The oxygenation process also appears to be equally applicable to upgrading existing overloaded activated sludge plants. It is believed that the aeration capacity of many overloaded systems can be increased 2-3 times without acquiring additional land for more aeration tanks. To test this hypothesis, the FWQA has recently awarded a $1.5 million Demonstration Grant to New York City for conversion of one existing 20 mgd bay of its Newtown Creek Plant to oxygen. The plant is currently accomplishing about 40% BOD removal with 1-1/2 hours of air aeration. It is hoped the removal efficiency of the test bay will be improved to 90% with oxygen. The test bay is scheduled to be on stream by late fall, 1971, and the grant evaluation will then continue for one year.

Other cities where Union Carbide is conducting non-federally sponsored pilot plant studies include Cincinnati, New Orleans, Louisville, Euclid, Ohio, Middlesex, New Jersey, and Speedway, Indiana.

AREAS NEEDING FURTHER INVESTIGATION

Questions remain to be answered concerning the following aspects of aeration with oxygen:

1. Nitrification: As mentioned previously, the Batavia experiments did not demonstrate nitrification. Definite criteria need to be established at which nitrification with oxygen can be guaranteed. Experiments are currently underway at the FWQA Blue Plains pilot plant in which a two-step oxygenation flow regime with intermediate clarification is being utilized to study this problem.

2. Sludge handling and disposal: The high solids concentrations and reduced quantities of waste activated sludge generated with oxygenation suggest several alternative approaches to anaerobic digestion for sludge disposal. Because of the highly oxidized condition of the sludge, several days of aerobic digestion may be sufficient to stabilize the sludge for land spreading. It may also be possible to dewater waste sludge directly from the clarifier underflow without any type of prior digestion. A follow-on contract for $208,714 was awarded to Union Carbide for further studies at Batavia during the summer and fall of 1970, a part of which included direct vacuum filtration of waste oxygenated sludge, aerobic stabilization of waste oxygenated sludge, and vacuum filtration of aerobically stabilized sludge. The final report from this follow-on contract will be available around May, 1971.

3. Carbon dioxide buildup in mixed liquor: Because of the closed aeration system, carbon dioxide (CO_2) tends to build up in solution in an oxygen aerator. At Batavia, this caused a drop

in mixed liquor pH of 0.5-0.7 units in all phases. Thus, it can be speculated that for stronger wastes more CO_2 will be produced and the drop in pH could be large enough to endanger the sludge culture.

Air Reduction Company is currently conducting a pilot study at the Greensboro, North Carolina South Buffalo Plant. In addition to domestic wastes, this plant receives all of the City's textile mill wastes. Organic strength of the combined municipal wastewater is very high. The Air Reduction oxygen aeration system uses a large diameter PVC pipe reactor to replace the standard open or closed aeration tank. Oxygen injection to the pipeline can be single or multi point as needed. The advantage of this system is that it requires no moving parts other than the prime mover for oxygen dissolution. If the pilot studies indicate the high strength wastewater can be effectively treated with oxygen, it is contemplated that the City of Greensboro will apply to FWQA for a Demonstration Grant, during which CO_2 buildup would be further investigated.

4. Effect of primary sedimentation: The effect of primary sedimentation on the oxygen process, particularly on sludge settling characteristics is not known. At this time, a recommendation for or against primary sedimentation in conjunction with oxygen aeration can not be made. The Newtown Creek Plant does not have primary settlers, so the answer to this question will have to come from privately funded studies or future federal grant projects.

CONCLUSIONS

1. Oxygen aeration is a highly oxidative process which operates effectively as a high rate system.
2. Significant reductions in waste activated sludge production are indicated with oxygen aeration.
3. Oxygen sludge settles and thickens well. It may be possible to dewater waste sludge from this process directly from the clarifier underflow.
4. The oxygen aeration process is applicable to both new and existing overloaded activated sludge plants.
5. Cost reductions in total treatment costs of 15-30% appear feasible for new plants with oxygen. Percent savings will be greater for conversion of existing overloaded plants to oxygen.

6. Several aspects of the oxygen aeration process require further investigation to maximize its full potential for waste treatment.

APPENDIX

All of the figures utilized in this discussion are reproduced directly from the final report of the Batavia project (6). Copies of this report can be obtained by writing to either of the following:

Planning and Resources Office
Office of Research and Development
Federal Water Quality Administration
U. S. Department of the Interior
Washington, D. C. 20242

Advanced Waste Treatment Research Laboratory
Federal Water Quality Administration
U. S. Department of the Interior
4676 Columbia Parkway
Cincinnati, Ohio 45226

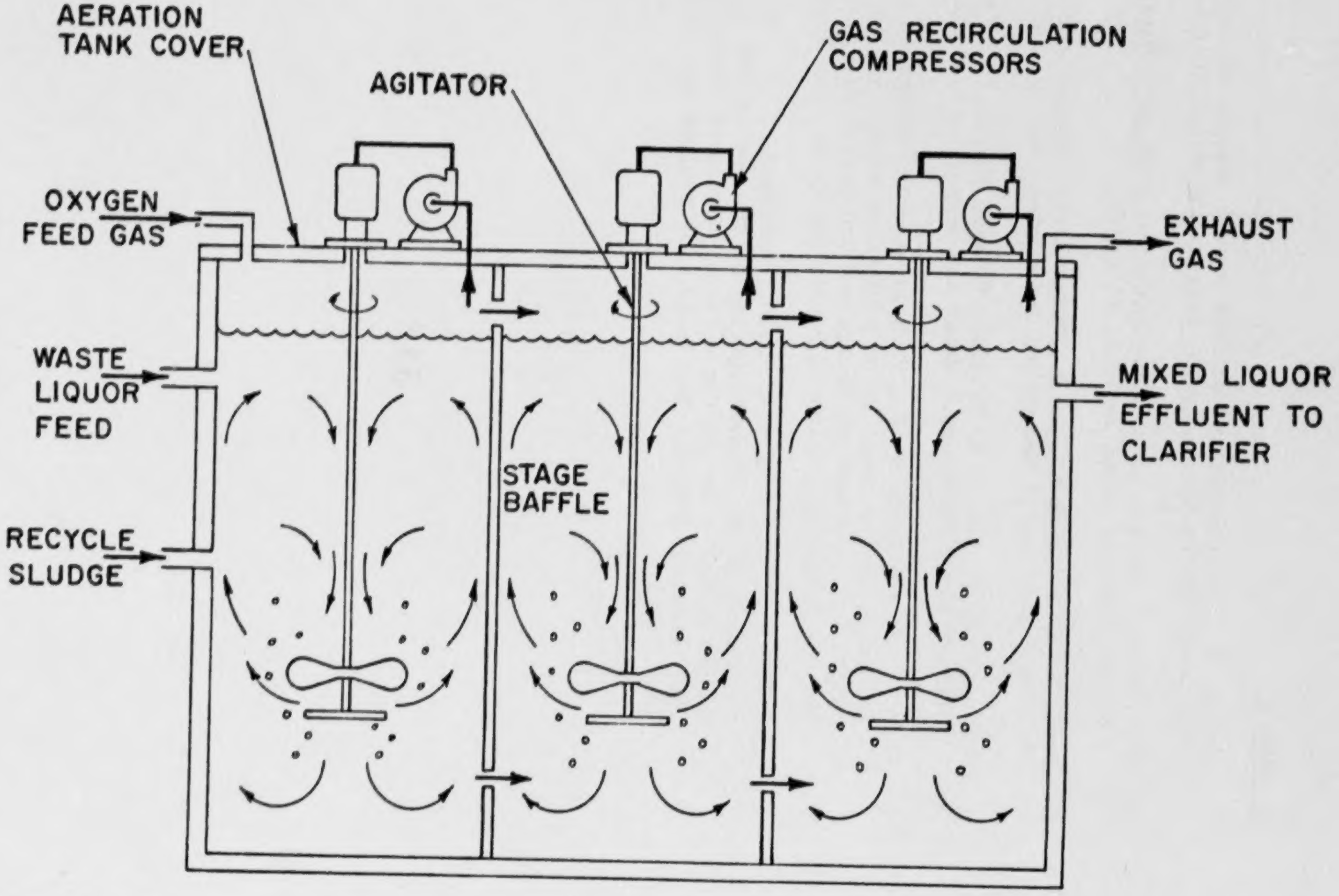
Attention: Mr. R. C. Brenner

REFERENCES

1. Pirnie, M., Paper presented at 21st Annual Meeting of Federation of Sewage Works Associations, Detroit, Michigan (October 1948).
2. Okun, D. A., "System of Bio-Precipitation of Organic Matter from Sewage," Sewage Works Journal, 21 (1949).
3. Budd, W. E. and Lambeth, G. F., "High Purity Oxygen in Biological Sewage Treatment," Sewage and Industrial Wastes, 29, 253 (1957).
4. McKinney, R. E. and J. T. Pfeffer, "Oxygen Enriched Air for Biological Waste Treatment," Water and Sewage Works (October 1965).
5. Okun, D. A. and Lynn, W. R., "Preliminary Investigation into the Effect of Oxygen Aeration on Biological Sewage Treatment," Biological Treatment of Sewage and Industrial Wastes: Volume I, Aerobic Oxidation, Reinhold Publishing Corp., New York (1956).
6. Albertsson, J. G., McWhirter, J. R., Robinson, E. K., and Vahldieck, N. P., "Investigation of the Use of High Purity Oxygen Aeration in the Conventional Activated Sludge Process," FWQA Research Contract No. 14-12-465, Program No. 17050 DNW (May 1970).

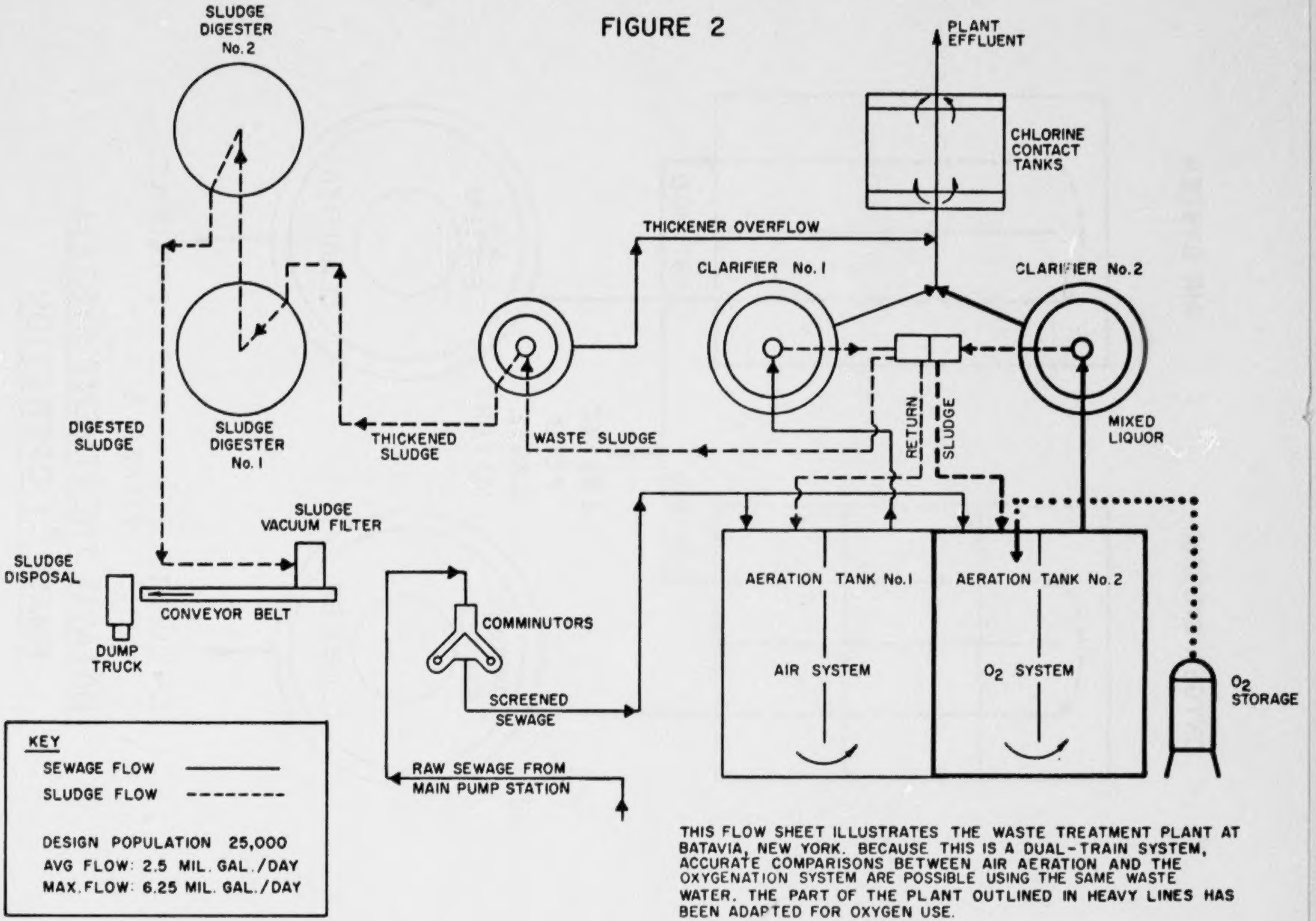
FIGURE I

SCHEMATIC DIAGRAM OF MULTI-STAGE
OXYGENATION SYSTEM


AERATION TANK COVER
AGITATOR
GAS RECIRCULATION COMPRESSORS
OXYGEN FEED GAS
EXHAUST GAS
WASTE LIQUOR FEED
MIXED LIQUOR EFFLUENT TO CLARIFIER
STAGE BAFFLE
RECYCLE SLUDGE

WATER POLLUTION CONTROL PLANT, CITY OF BATAVIA, N.Y.
SCHEMATIC FLOW DIAGRAM

FIGURE 2


SLUDGE DIGESTER No. 2
PLANT EFFLUENT
CHLORINE CONTACT TANKS
THICKENER OVERFLOW
CLARIFIER No. 1
CLARIFIER No. 2
SLUDGE DIGESTER No. 1
DIGESTED SLUDGE
THICKENED SLUDGE
WASTE SLUDGE
RETURN
SLUDGE
MIXED LIQUOR
SLUDGE VACUUM FILTER
SLUDGE DISPOSAL
CONVEYOR BELT
DUMP TRUCK
COMMINUTORS
SCREENED SEWAGE
RAW SEWAGE FROM MAIN PUMP STATION
AERATION TANK No. 1
AIR SYSTEM
AERATION TANK No. 2
O_2 SYSTEM
O_2 STORAGE
KEY
SEWAGE FLOW
SLUDGE FLOW
DESIGN POPULATION 25,000
AVG FLOW: 2.5 MIL. GAL./DAY
MAX. FLOW: 6.25 MIL. GAL./DAY

THIS FLOW SHEET ILLUSTRATES THE WASTE TREATMENT PLANT AT BATAVIA, NEW YORK. BECAUSE THIS IS A DUAL-TRAIN SYSTEM, ACCURATE COMPARISONS BETWEEN AIR AERATION AND THE OXYGENATION SYSTEM ARE POSSIBLE USING THE SAME WASTE WATER. THE PART OF THE PLANT OUTLINED IN HEAVY LINES HAS BEEN ADAPTED FOR OXYGEN USE.

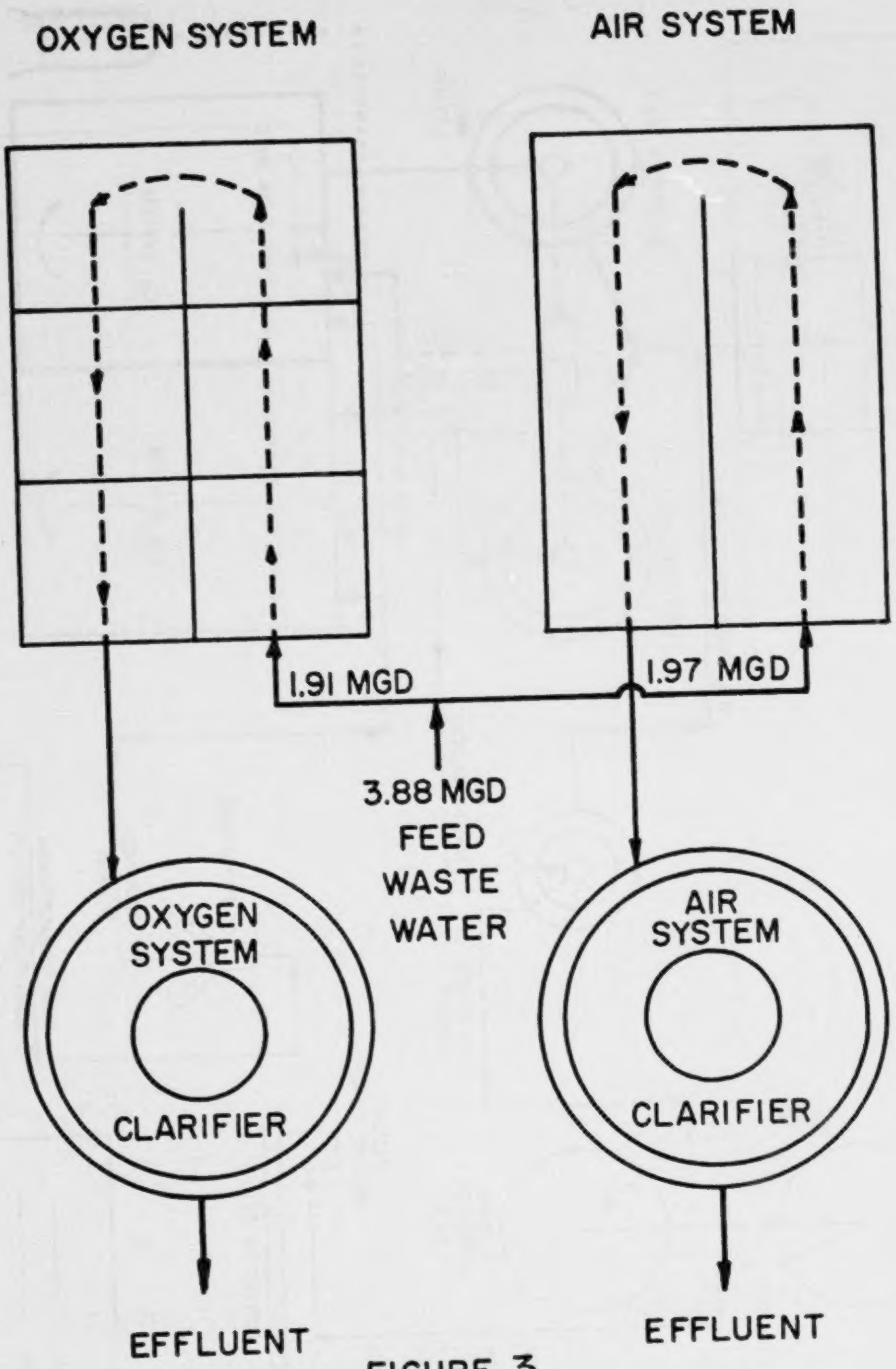

OXYGEN SYSTEM
AIR SYSTEM
1.91 MGD
1.97 MGD
3.88 MGD
FEED
WASTE
WATER
OXYGEN
SYSTEM
CLARIFIER
AIR
SYSTEM
CLARIFIER
EFFLUENT
EFFLUENT

FIGURE 3

BATAVIA TREATMENT SYSTEM
PHASE # I OPERATION

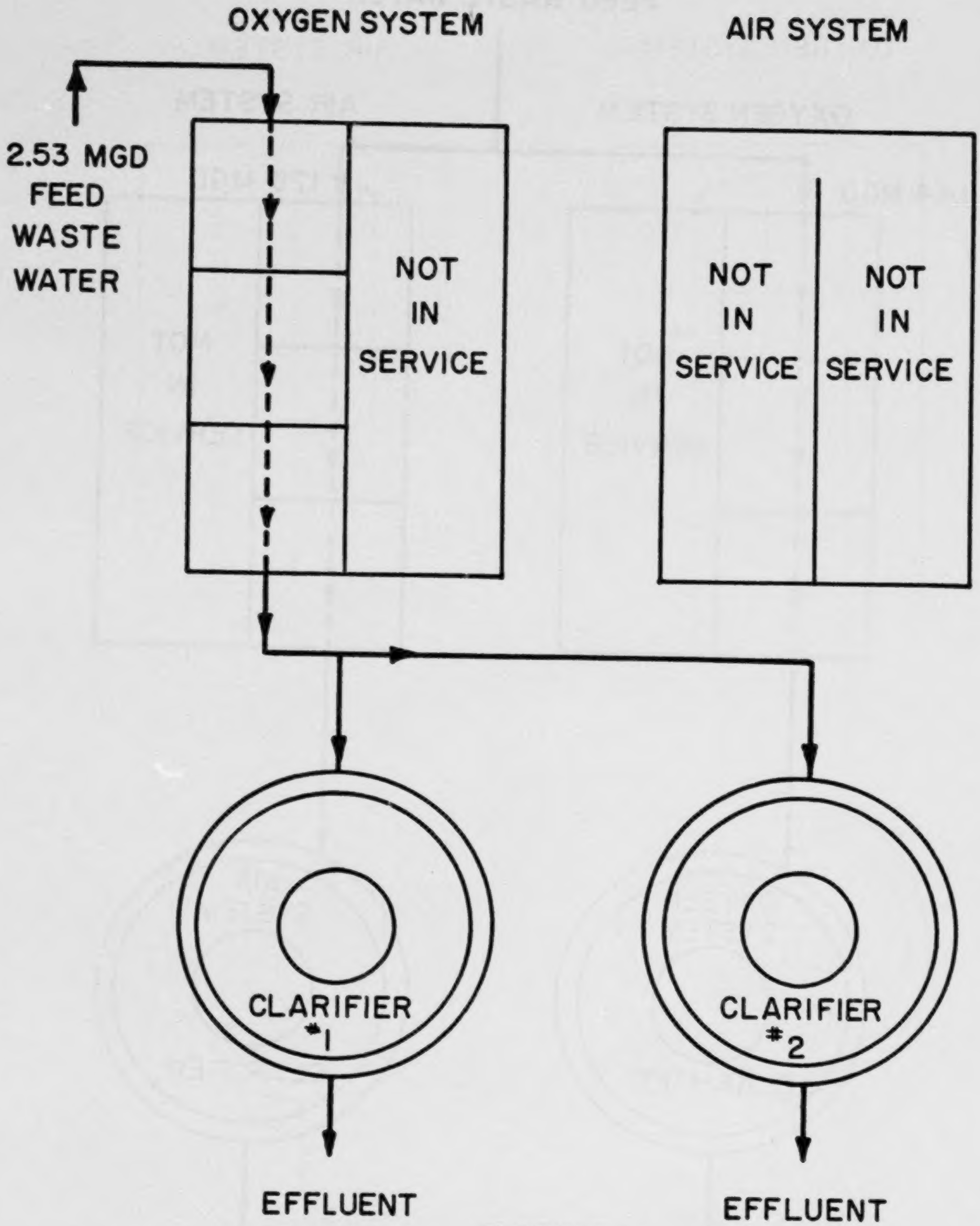

OXYGEN SYSTEM
AIR SYSTEM
2.53 MGD
FEED
WASTE
WATER
NOT
IN
SERVICE
NOT
IN
SERVICE
NOT
IN
SERVICE
CLARIFIER
#1
CLARIFIER
#2
EFFLUENT
EFFLUENT

FIGURE 4

BATAVIA TREATMENT SYSTEM
PHASE #2 OPERATION

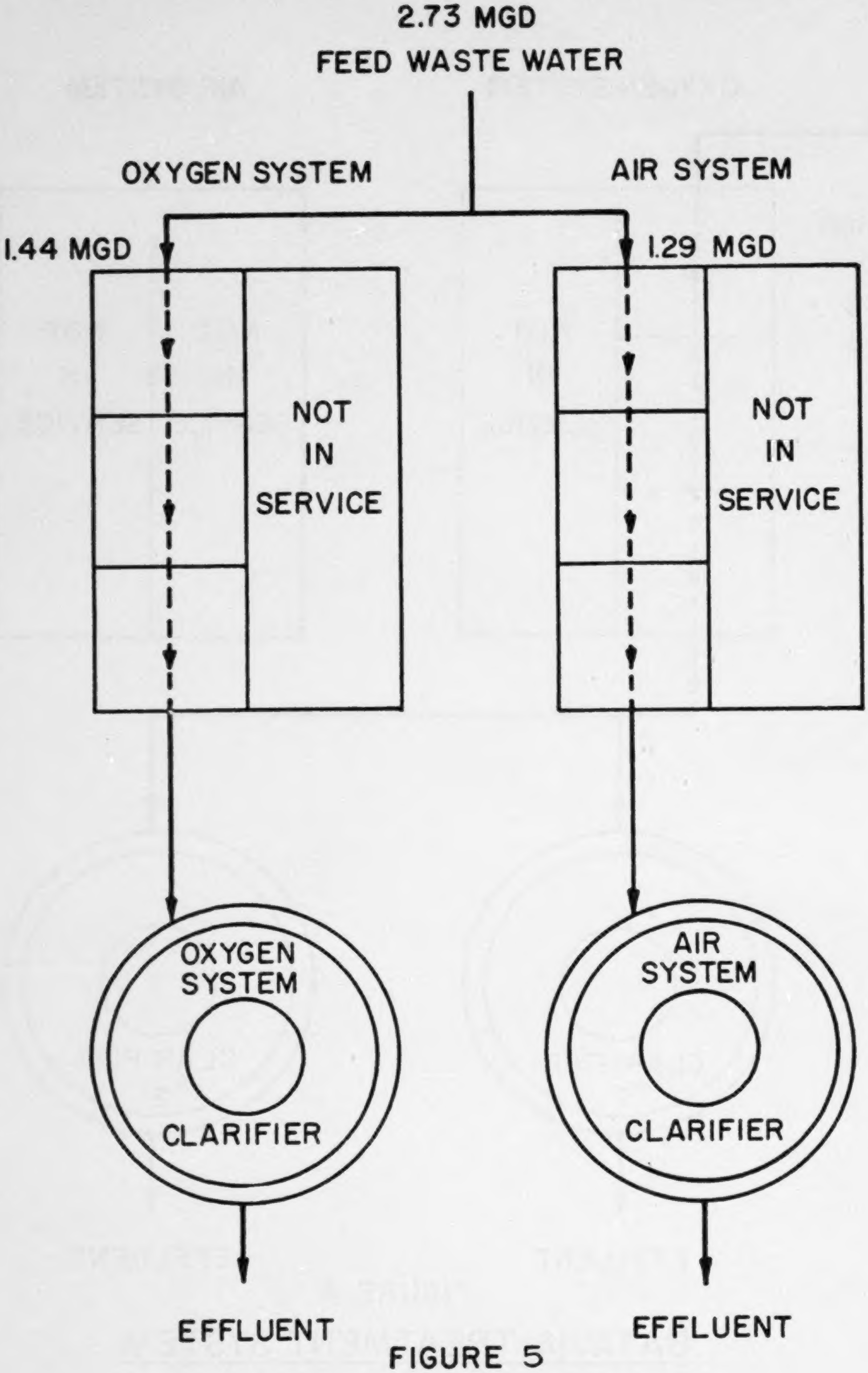

2.73 MGD
FEED WASTE WATER
OXYGEN SYSTEM
AIR SYSTEM
1.44 MGD
1.29 MGD
NOT IN SERVICE
NOT IN SERVICE
OXYGEN SYSTEM
CLARIFIER
AIR SYSTEM
CLARIFIER
EFFLUENT
EFFLUENT

FIGURE 5

BATAVIA TREATMENT SYSTEM
PHASE # 3 OPERATION

FIGURE 6

COMPARATIVE SUMMARY OF AIR AND OXYGENATION TREATMENT SYSTEM PERFORMANCE

	Phase I Operation		Phase II Operation	Phase III Operation	
	Air System	Oxygenation System	Oxygenation System	Air System	Oxygenation System
Wastewater Feed Rate (MGD)	1.97	1.91	2.53	1.29	1.44
Sludge Recycle Rate (MGD)	0.25	0.44	0.83	0.25	0.60
Recycle Sludge/Wastewater Feed Rate Ratio	0.13	0.24	0.34	0.21	0.45
Wastewater Temperature (°F)	59	59	66	70	70
Mixed-liquor average D.O. Conc.(mg/l)	1.5	8.7	9.0	0.8	8.0
Clarifier Effluent D.O. Conc. (mg/l)	0.4	4.0	0.7	0	4.3
*Aeration Detention Time (hrs.)	3.5	3.4	1.2	2.6	2.0
**Nominal Aeration Detention Time (hrs.)	4.0	4.1	1.5	3.0	2.8
MLSS Concentration (mg/l)	2440	3060	6980	3640	6190
MLVSS Concentration (mg/l)	1740	2210	4450	2580	4310
Recycle Sludge TSS (mg/l)	14,960	18,620	29,560	16,600	18,790
Recycle Sludge VSS (mg/l)	9,710	11,760	18,180	11,840	12,720
Recycle Sludge VSS/TSS Ratio	0.65	0.63	0.62	0.71	0.69
Mixed-liquor Sludge Volume Index	76	64	36	63	49
Mixed-liquor Initial Settling Velocity, (ft/hr)	7.7	7.2	6.5	7.7	5.1
Final Clarifier Overflow Rate as gal/ft^2/day	1570	1520	1010	1030	1140

* Raw flow plus recycle sludge flow.

** Raw wastewater flow only.

FIGURE 7

COMPARATIVE SUMMARY OF AIR AND OXYGENATION TREATMENT SYSTEMS PERFORMANCE

	Phase I Operation		Phase II Operation	Phase III Operation	
	Air System	Oxygenation System	Oxygenation System	Air System	Oxygenation System
Feed Wastewater BOD (mg/l)	159	159	220	262	262
Clarifier Effluent BOD (mg/l)	16	11	23	30	14
% BOD Removal	90	92	90	88	94
Feed Wastewater COD (mg/l)	352	352	325	578	578
Clarifier Effluent COD(mg/l)	84	73	97	116	89
% COD Removal	76	80	71	79	84
Feed Wastewater TSS (mg/l)	221	221	174	430	430
Clarifier Effluent TSS (mg/l)	16	9	19	23	12
% TSS Removal	93	96	89	94	97
Feed Wastewater VSS (mg/l)	152	152	123	332	332
Effluent Turbidity (J.T.U.)	5.7	5.6	9.1	5.7	4.4
Food/Biomass Ratio as lbs.BOD/Day/lb. MLVSS	0.566	0.414	0.790	0.841	0.554
Volumetric Organic Loading as lbs.BOD/day/1000 ft^3 mixed-liquor	60.0	57.9	212.5	128.9	144.8
Lbs. Dry Solids Wasted/Day	3148	1804	2448	3494	592
Lbs. VSS Wasted per Lb. BOD Removed	0.871	0.482	0.412	0.989	0.134

FIGURE 8.

COMPARATIVE SUMMARY OF AIR AND OXYGENATION TREATMENT SYSTEMS PERFORMANCE

	Phase I Operation		Phase II Operation	Phase III Operation	
	Air System	Oxygenation System	Oxygenation System	Air System	Oxygenation System
Feed Wastewater Total Phosphate (mg/l)	11	11	12	19	19
Clarifier Effluent Total Phosphate (mg/l)	6	7	10	13	14
% Total Phosphate Removed	44	39	12	32	27
Feed Wastewater NH_3-N (mg/l)	20	20	19	30	30
Clarifier Effluent NH_3-N (mg/l)	17	15	18	24	24
Feed Wastewater TKN (mg/l)	34	34	33	53	53
Clarifier Effluent TKN (mg/l)	22	19	22	31	30
Feed Wastewater NO_2-N (mg/l)	0.2	0.2	0	0	0
Clarifier Effluent NO_2-N(mg/l)	0.4	0.9	0.2	0.2	0.7
Feed Wastewater NO_3-N (mg/l)	0.3	0.3	0.1	0.1	0.1
Clarifier Effluent NO_3-N (mg/l)	0.6	1.6	1.7	2.2	2.5
Feed Wastewater Total Nitrogen (mg/l)	35	35	34	53	53
Clarifier Effluent Total Nitrogen(mg/l)	23	21	26	33	33
% Total Nitrogen Removed	35	37	23	36	36
NO_3-Nitrogen/Total Nitrogen in Clarifier Effluent	0.03	0.08	0.07	0.07	0.07
Lbs. Total Nitrogen Removed per Lb. Dry Solids Wasted	0.066	0.129	0.066	0.060	0.453

FIGURE 9.

COMPARATIVE SUMMARY OF AIR AND OXYGENATION TREATMENT SYSTEMS PERFORMANCE

	Phase I Operation		Phase II Operation	Phase III Operation	
	Air System	Oxygenation System	Oxygenation System	Air System	Oxygenation System
Ft^3 Air Utilized/gal. Sewage Treated	2.89	-	-	4.32	-
Feed Oxygen Flow Rate (cfm,NTP)	-	18.3	31.0	-	19.0
Gas Exhaust Rate from Oxygen System Final Stage (cfm,NTP)	-	1.74	4.04	-	3.22
Oxygen System Exhaust Gas Composition as % Oxygen	-	46	55	-	51
Overall % of Feed Oxygen Utilized	-	95.5	92.7	-	91.4
Lbs. Oxygen Utilized/Lb. BOD Consumed	-	0.94	0.96	-	0.72
Total Power Required for Liquid Mixing (HP)	-	26.0	11.1	-	11.7
Total Power Required for Gas Recirculation (HP)	-	2.6	9.2	-	10.6
Overall Power Utilized as HP per 1000 Gal. Mixed-liquor	-	0.088	0.125	-	0.137
Total Air Blower Power Utilized (HP)	141	-	-	138.5	-

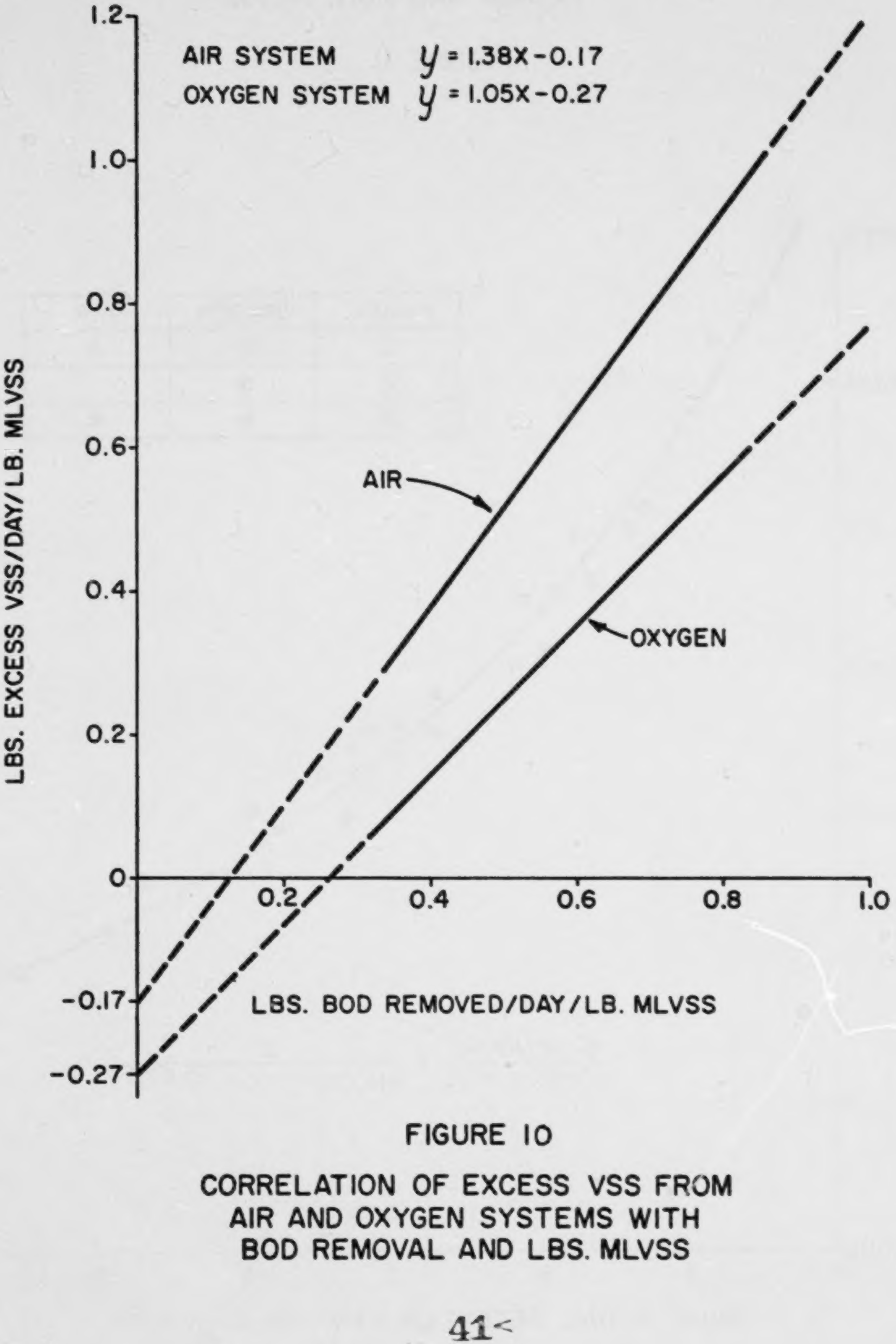


FIGURE 10

CORRELATION OF EXCESS VSS FROM AIR AND OXYGEN SYSTEMS WITH BOD REMOVAL AND LBS. MLVSS

CORRELATION OF % BOD REMOVAL AT BATAVIA WITH ACTUAL DETENTION PERIOD AND MG/L MLVSS

FIGURE 11

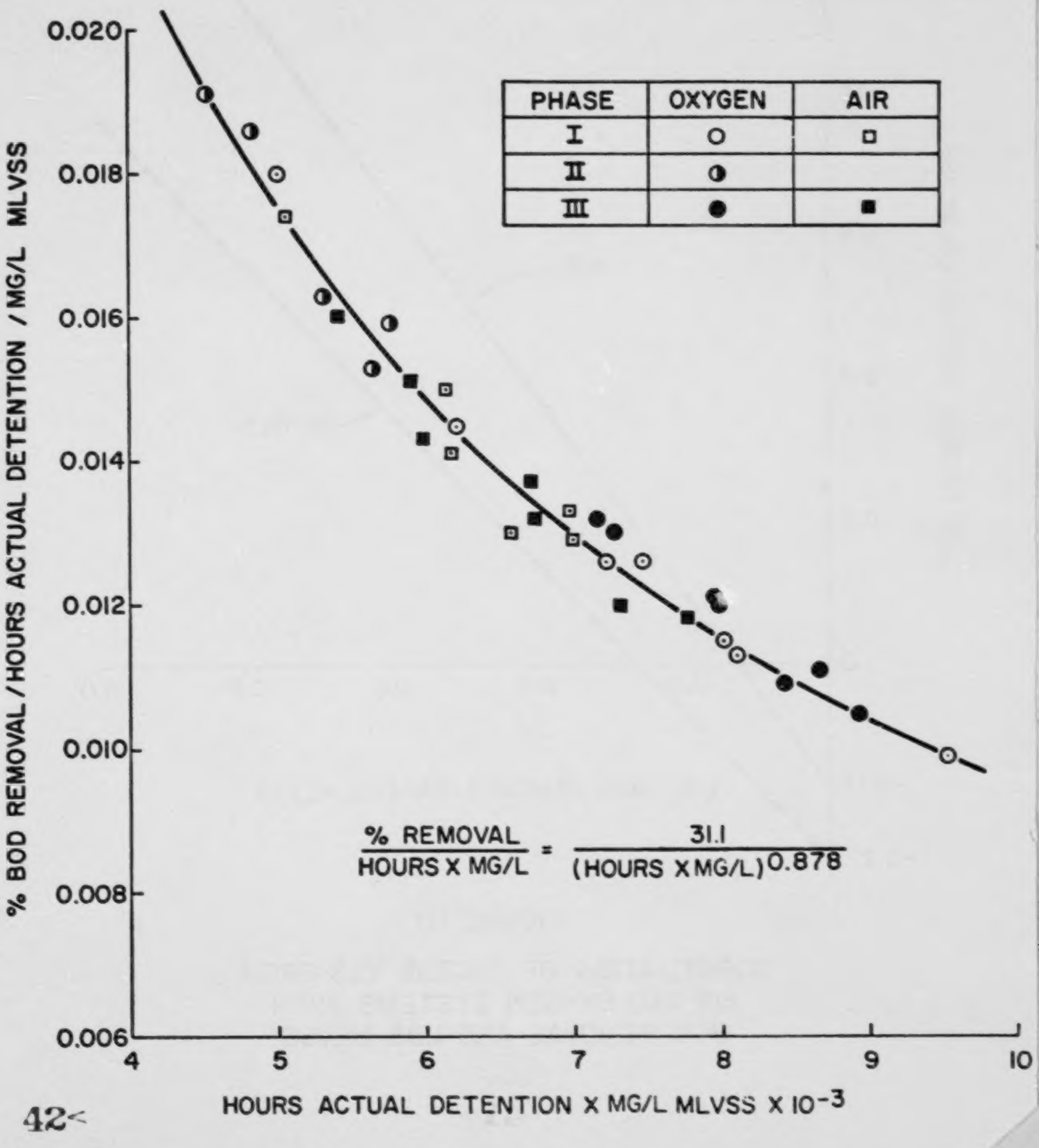


FIGURE 12

SUMMARY OF AERATION RESIDENCE TIMES AND BOD REMOVALS FOR AIR AND OXYGENATION SYSTEM ECONOMIC COMPARISONS

Air System Aeration Detention Time-Hrs. (based on Raw Flow)	Percent BOD Removal Secondary System	Oxygen System Aeration Detention Time-Hrs. (based on Raw Flow)
3.0	84	1.00
4.0	87	1.33
5.0	90	1.66
6.0	92	2.00

FIGURE 13.

SUMMARY OF VOLUMETRIC ORGANIC LOADINGS AND FOOD TO BIOMASS RATIOS FOR AIR AND OXYGENATION SYSTEM DESIGNS

Aeration Detention Time-Hrs(based on raw flow)	MLVSS Conc. mg/l	Volumetric Organic Loading (lbs BOD/Day 1000 ft^3)	Food to Biomass Ratio (lb BOD/Day lb MLVSS)
		OXYGENATION SYSTEM	
1.00	4420	194	.70
1.33	4420	146	.53
1.66	4420	117	.42
2.00	4420	97	.35
		AIR SYSTEM	
3.0	1625	65	.64
4.0	1625	49	.48
5.0	1625	39	.38
6.0	1625	32	.32

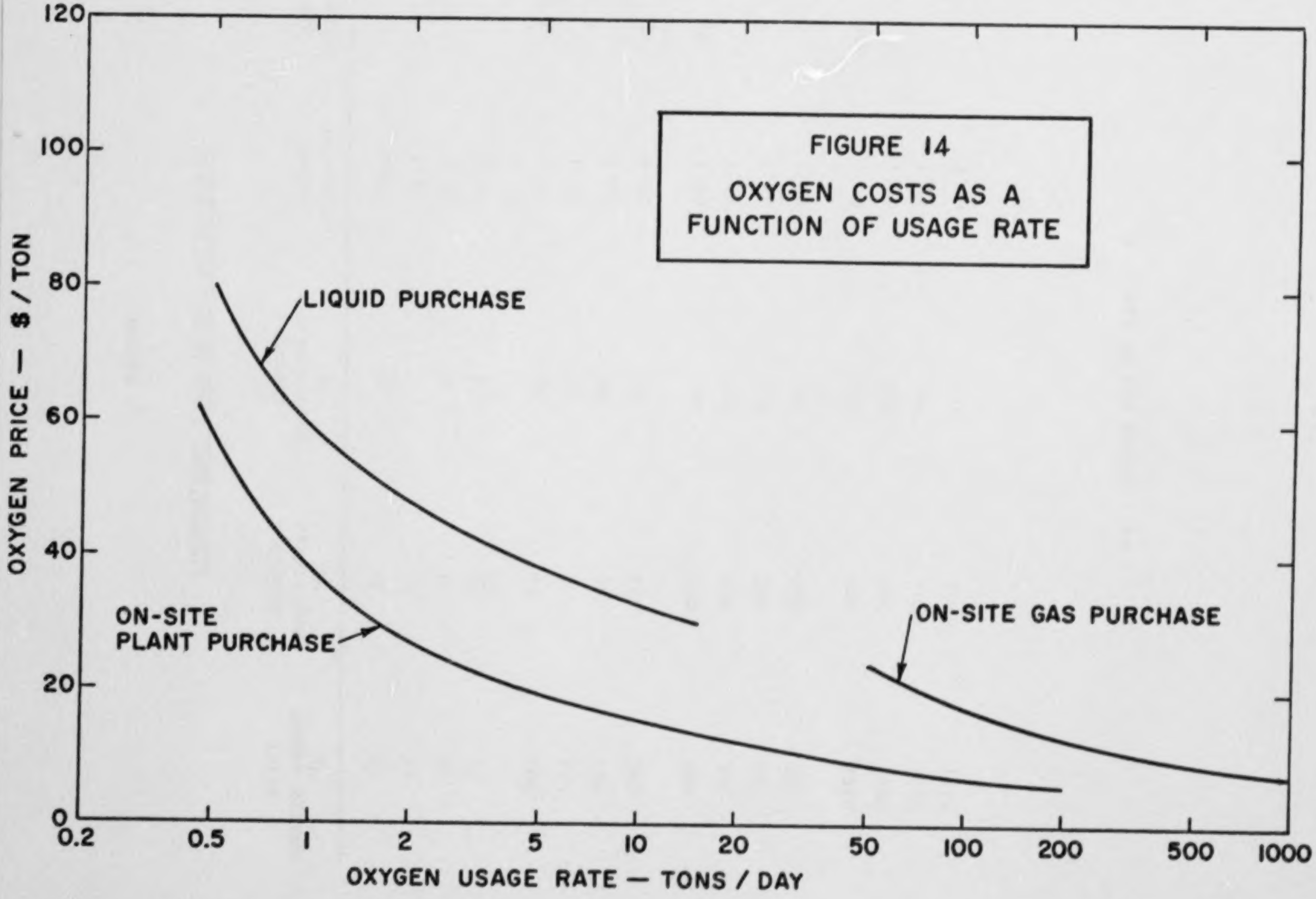


FIGURE 14
OXYGEN COSTS AS A
FUNCTION OF USAGE RATE

FIGURE 15

OXYGENATION SYSTEM POWER REQUIREMENTS

MGD Treated	*Hours Detention	Oxygen Dissolution HP	Oxygen Generation HP	Total Oxygen System HP
1	1.00	6	11	17
	1.33	7	12	19
	1.66	8	14	22
	2.00	10	15	25
6	1.00	37	63	100
	1.33	43	70	113
	1.66	50	78	128
	2.00	57	85	142
30	1.00	180	300	480
	1.33	210	350	560
	1.66	250	385	635
	2.00	280	420	700
100	1.00	510	800	1310
	1.33	620	900	1520
	1.66	740	1000	1740
	2.00	870	1090	1960

* Based on Raw Sewage Flow

FIGURE 16

DIFFUSED AIR AERATION POWER REQUIREMENTS

	BLOWER HP REQUIRED		
MGD TREATED	0.8 CF (NTP) OF AIR PER GAL. OF SEWAGE	1.6 CF (NTP) OF AIR PER GAL. OF SEWAGE	2.4 CF (NTP) OF AIR PER GAL. OF SEWAGE
1	25	50	75
6	150	295	440
30	735	1470	2200
100	2450	4880	7350

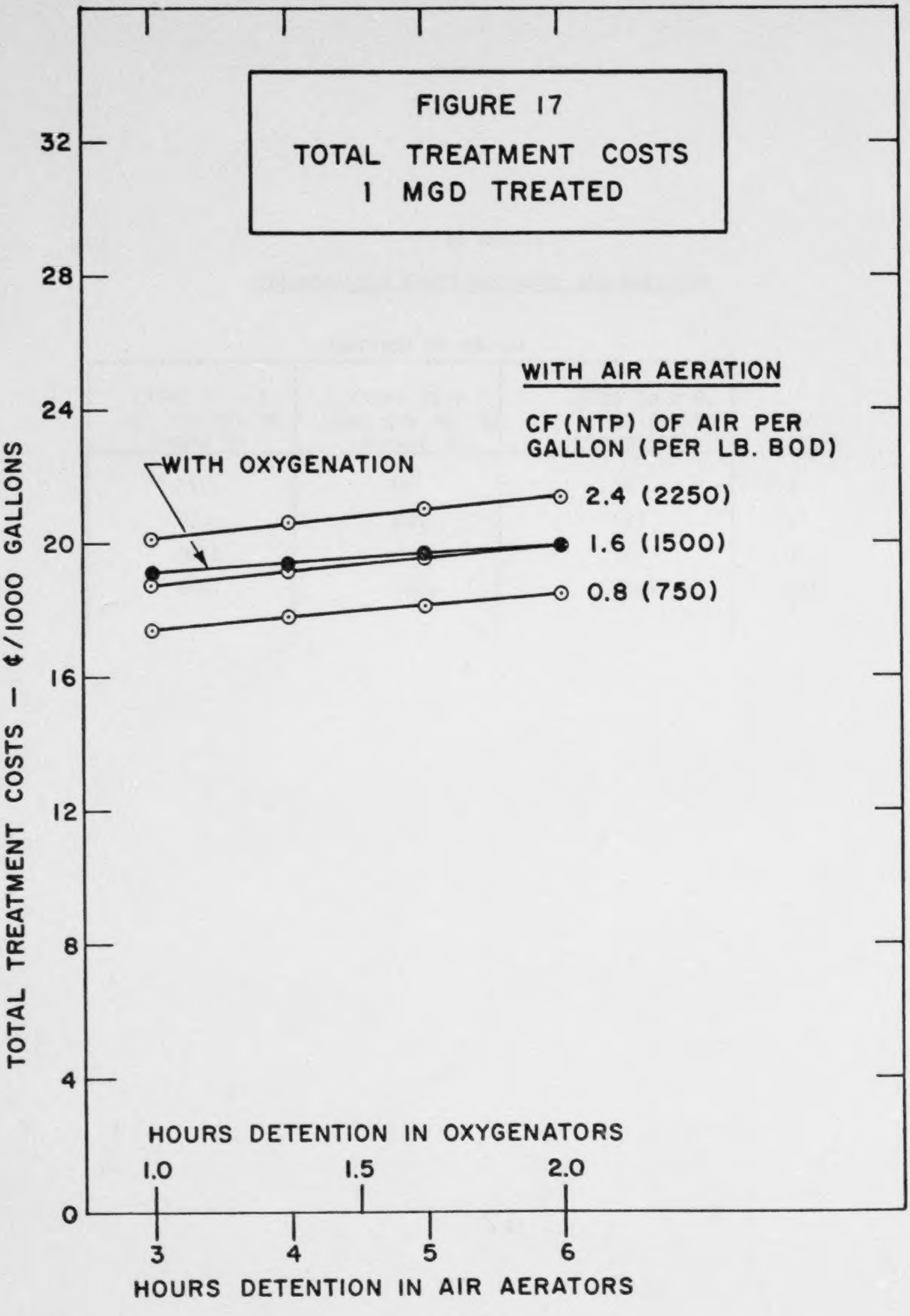


FIGURE 17

TOTAL TREATMENT COSTS

1 MGD TREATED

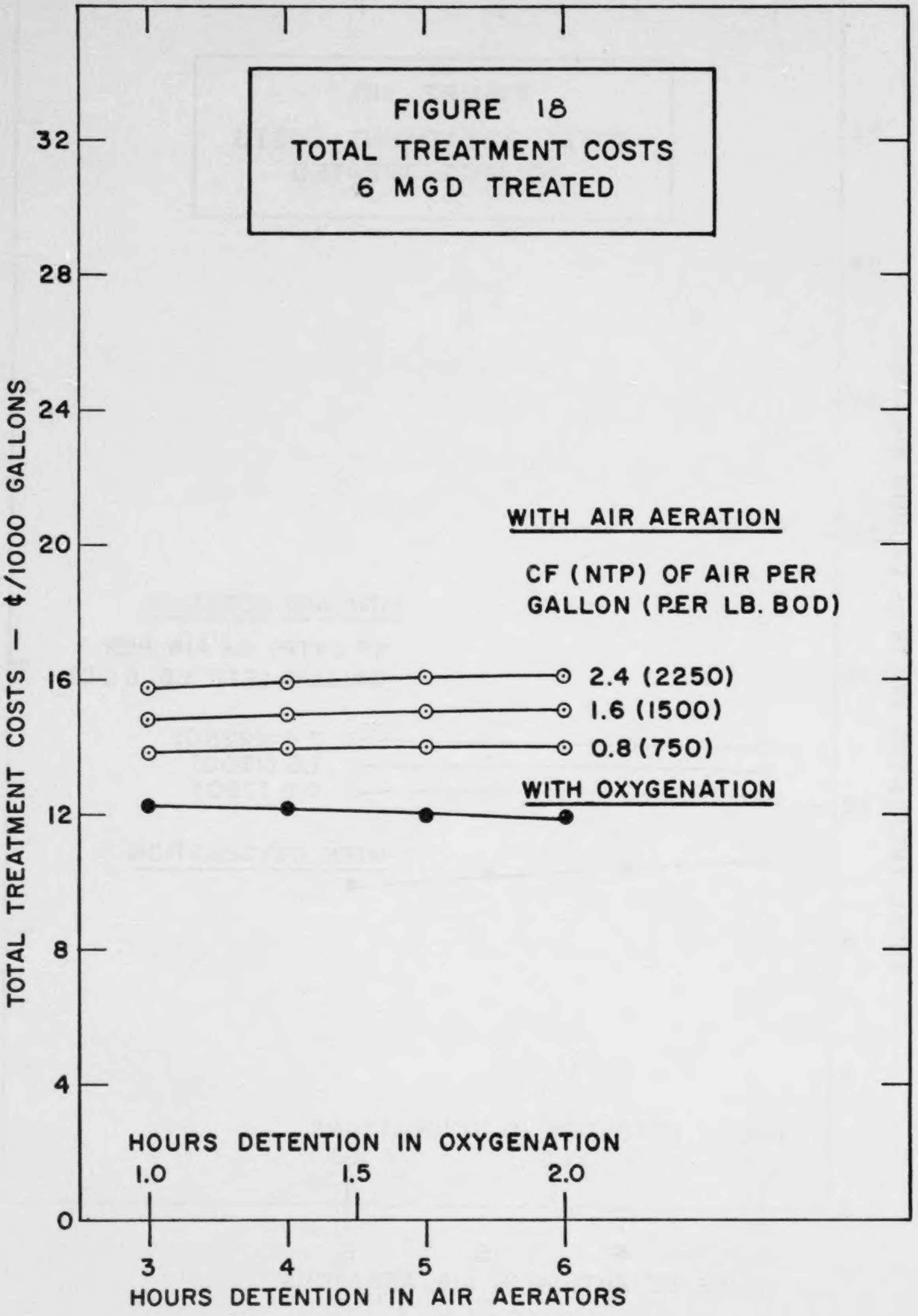


FIGURE 18
TOTAL TREATMENT COSTS
6 MGD TREATED

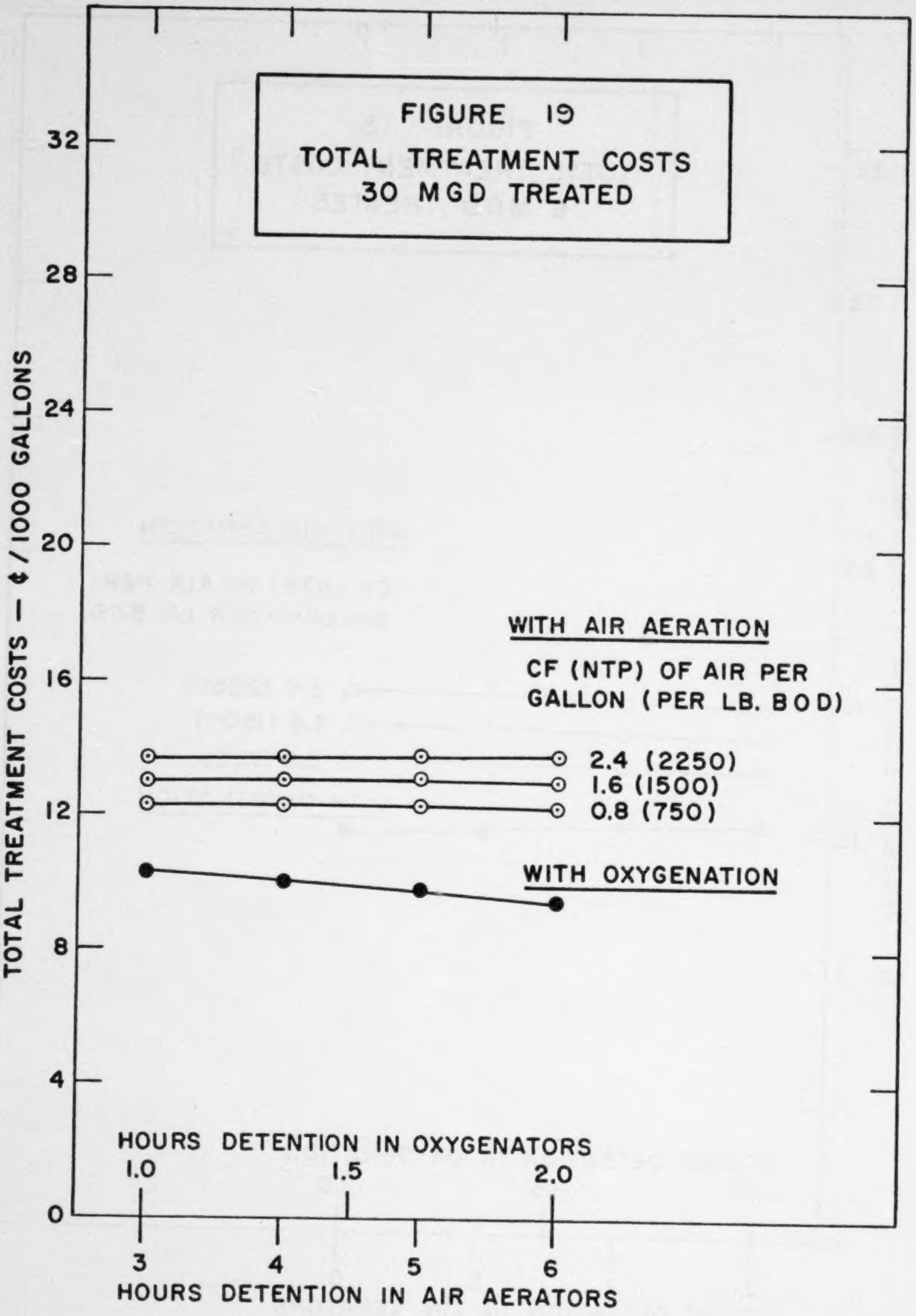


FIGURE 19
TOTAL TREATMENT COSTS
30 MGD TREATED

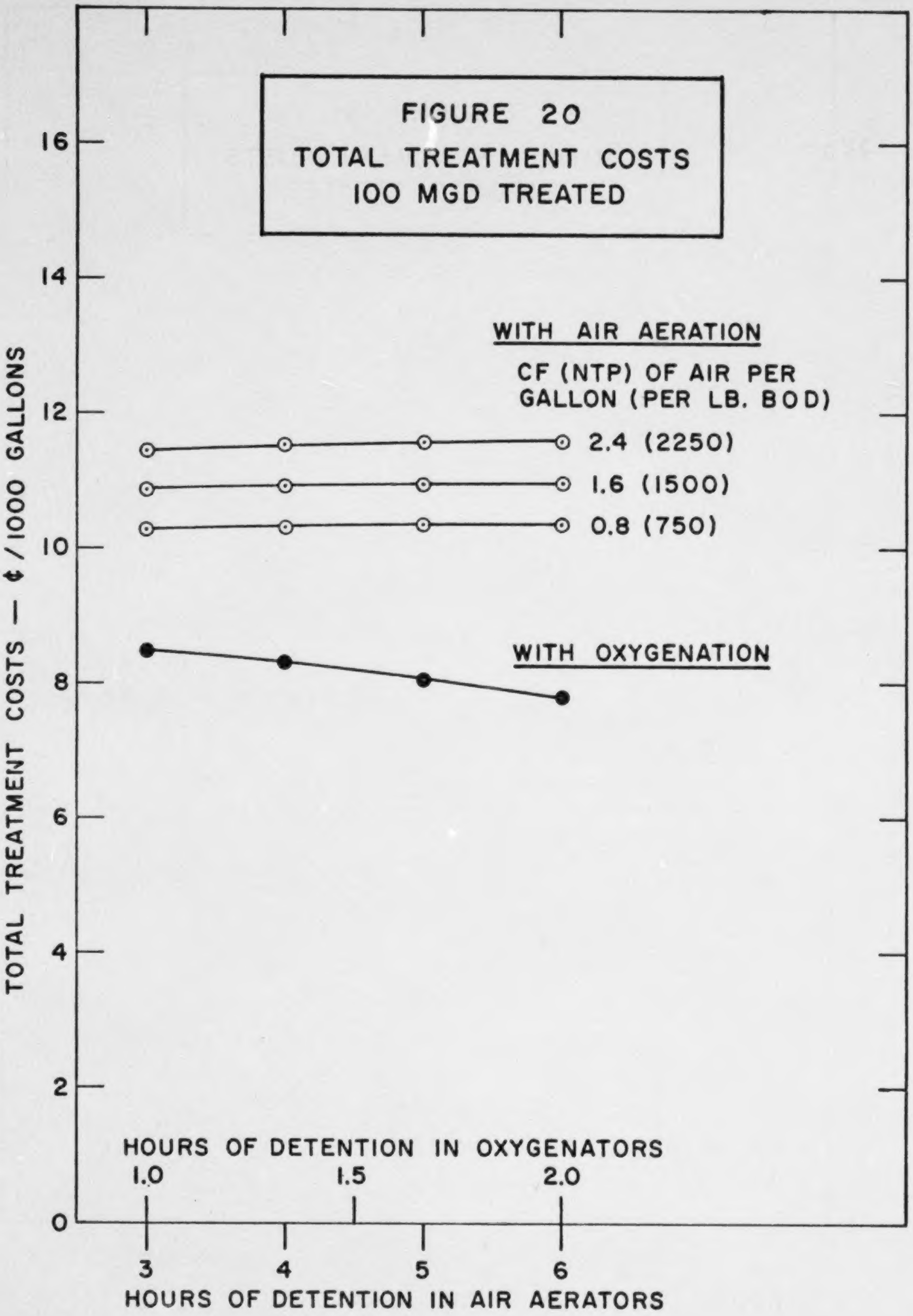
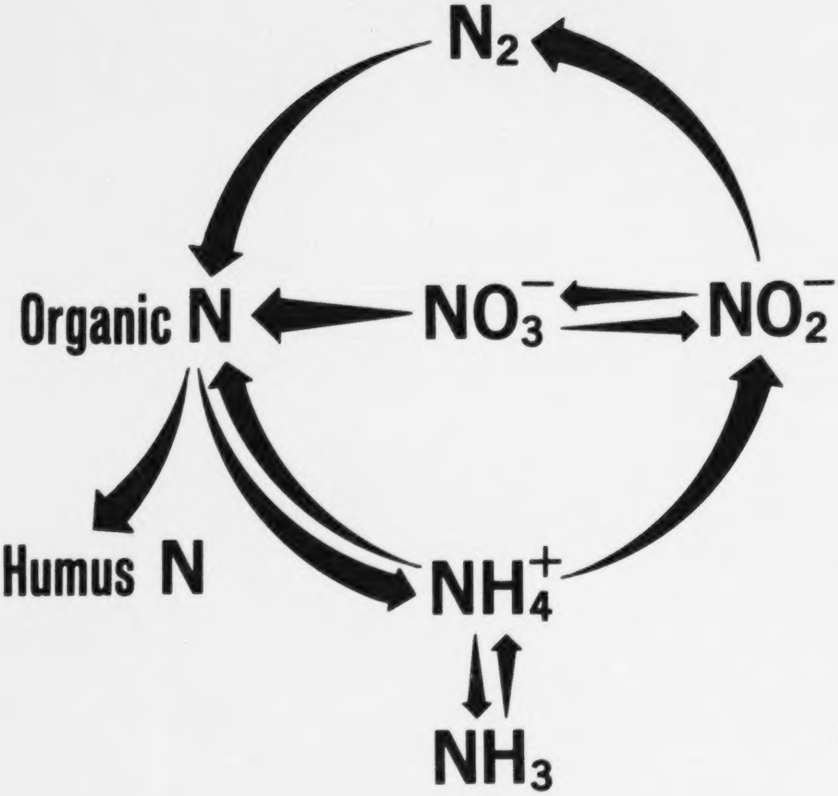


FIGURE 20
TOTAL TREATMENT COSTS
100 MGD TREATED

ORD-17010 --- 10/70

NITROGEN REMOVAL FROM WASTEWATERS


N_2
Organic N
NO_3^-
NO_2^-
Humus N
NH_4^+
NH_3

FEDERAL WATER QUALITY ADMINISTRATION
DIVISION OF RESEARCH AND DEVELOPMENT
ADVANCED WASTE TREATMENT RESEARCH LABORATORY
CINCINNATI, OHIO
OCTOBER 1970

52<

WATER POLLUTION CONTROL RESEARCH SERIES

The Water Pollution Control Research Reports describe the results and progress in the control and abatement of pollution of our Nation's waters. They provide a central source of information on the research, development, and demonstration activities of the Federal Water Quality Administration, Department of the Interior, through in-house research and grants and contracts with Federal, State, and local agencies, research institutions, and industrial organizations.

Water Pollution Control Research Reports will be distributed to requesters as supplies permit. Requests should be sent to the Planning and Resources Office, Office of Research and Development, Federal Water Quality Administration, Department of the Interior, Washington, D. C. 20242.

NOTE:

This booklet is a specialized edition for the Dallas, Texas, January 12, 13, and 14, 1971 Symposium.

Material presented by Dr. J. Farrell and Mr. E. Barth in Session No. 2, January 12, is included. Also, other topics not covered in the oral presentations are provided for your information.

FOREWORD

Classically, sewage treatment has been directed toward the removal of suspended solids, biochemical oxygen demand and reduction of bacterial contaminants. Removal of nutrients such as phosphorus and nitrogen has been incidental to treatment processes. The rapid increase in severe eutrophication problems in recent years has focused attention on nutrient control from municipal sources.

Phosphorus removal techniques, as a result of extensive research over the past several years, are now useable by cities and are awaiting the extensive application that is expected. Nitrogen transformation or removal from most wastewaters will have to be accomplished. In some instances, converting ammonia to nitrates will be sufficient; in other cases, full nitrogen removal will be required.

Full scale treatment plants designed for nitrogen removal are not yet in operation in the United States. A full scale (50 mgd) plant to convert ammonia to nitrate is being designed. Biological denitrification can be designed when needed. The Advanced Waste Treatment Research Laboratory has conducted and sponsored much of the current research on nitrogen removal. This report, assembled by Dr. Robert B. Dean with the assistance of several staff members, provides a state of the knowledge on nitrogen removal that is current as of October 1, 1970. This report supersedes an earlier report dated May, 1970.

F. M. Middleton
Director of Research
Advanced Waste Treatment
Research Laboratory

from
p. 17

NITROGEN REMOVAL FROM WASTEWATERS

INDEX

	Foreword	
	Abstract	
1.	Nitrogen Removal from Wastewaters--Statement of the Problem	Barth and Dean
2.	Nitrogen Removal by Biological Suspended Growth Reactors	Barth
3.	Nitrogen Removal from Wastewaters by Column Reactors	Smith
4.	Ammonia Nitrogen Removal by Stripping with Air	Farrell
5.	Removal of Ammonia Nitrogen by Selective Ion Exchange	Dean
6.	Ion Exchange for Nitrate Removal	Dobbs
7.	Other Methods for Removing Nitrogen	Dean
8.	Salt Creek Two Stage Nitrification Plant	Woodward
	Bibliography	

NITROGEN REMOVAL FROM WASTEWATERS

Edited by Robert B. Dean
Advanced Waste Treatment Research Laboratory
Robert A. Taft Water Research Center

ABSTRACT

Ammonia and nitrates are the principal forms of nitrogen in wastewaters. Ammonia is converted to nitrates by biological oxidation. Because of this reaction it exerts a high BOD in surface waters. Nitrates are reduced to nitrogen gas by bacteria when organic matter exceeds the oxygen supply. Both compounds are algal nutrients but ammonia is much more toxic than nitrates. The best developed method for control of nitrogen compounds is biological oxidation to nitrates followed by denitrification with the aid of methanol.

Ammonia stripping at high pH in cooling towers following lime treatment is effective but cannot be used during freezing weather and may suffer from serious scale problems. Selective ion exchange of ammonia with lime regeneration may be practical but the process is still in the pilot stage. Several other processes are being studied. A bibliography of pertinent references is attached.

Paper No. 1

NITROGEN REMOVAL FROM WASTEWATERS -- STATEMENT OF THE PROBLEM

Edwin F. Barth and Robert B. Dean

Nitrogen is continuously cycled through the environment from the atmosphere to growing plants and back to nitrogen gas. The principal species are presented in the classical nitrogen cycle as shown on the cover. Fixation of nitrogen to produce organic nitrogen is carried out by specialized bacteria, algae and a few higher plants. When these organisms decompose much of the organic nitrogen is converted to ammonia. A small fraction however is converted to relatively stable humus nitrogen in the soil. Ammonia and ammonium ion are rapidly interconvertible and the ratio of the two species depends on the pH according to the equation:

1) $\log (NH_3/NH_4) = pH - 9.25$ at 25°

Minor corrections to this equation are necessary in brackish waters and at low or high temperatures. Below pH 7.25 less than 1% of ammonia is present as NH_3.

Ammonia is nitrified or converted to nitrates by two specialized groups of bacteria. Nitrosomonas oxidizes ammonia to nitrite and Nitrobacter oxidizes nitrite to nitrate. Oxygen is required as well as CO_2 for bacterial growth but dissolved organic matter has little or no influence. Nitrifiers are very sensitive to poisoning by many simple substances including heavy metals and free ammonia. Biological nitrification of industrial wastes can therefore not be assumed without careful testing under realistic conditions.

Nitrates can be reduced by many bacteria that use the oxygen for metabolism. Nitrites are the first product but they are usually rapidly reduced to nitrogen gas by further bacterial action. Nitrates can also be utilized as a source of nitrogen by most growing plants.

The nitrogen content of natural unpolluted waters is normally less than one milligram per liter, and during the growing season, soluble nitrogen compounds are virtually completely depleted by growing plants and algae (AWWA, 1970).* The presence of nitrogen compounds, particularly ammonia, has therefore been taken as an indication of pollution for over a century. Historically, nitrogen analyses have seniority over BOD_5 and suspended solids determinations to trace wastewater pollution and to control biological treatment. The BOD_5 tests replaced tests for various nitrogen compounds for two reasons. First, analysis was not as tedious; and secondly, the BOD_5 tests made biological processes look more efficient, since it is much easier to get 85% reduction of BOD than it is to get a comparable conversion to nitrates.

Municipal wastewaters have nitrogen contents in the 15-25 mg/l range in untreated and primary settled wastes; the nitrogen is divided between organic compounds, which are mostly insoluble, and ammonia. Biological treatment converts most of the organic nitrogen to ammonia, and under favorable conditions ammonia may be oxidized to nitrates. Nitrogen compounds of lesser significance are discussed in paper No. 7.

The conditions for nitrification of municipal effluents have been worked out by Downing and Hopwood (1964) who showed that

> "to achieve nitrification consistently, the period of aeration must exceed a minimum value which is a function of the concentration of activated sludge, the temperature, and the strength of the sewage. When conditions are favourable for nitrification, the rate of nitrification and the rate of consumption of oxygen due to this process will tend to an equilibrium level which is proportional to the concentration of activated sludge under aeration. In an aeration unit through which the liquid travels with ideal piston-flow, the concentration of ammonia in the effluent under the above conditions will be normally very small. The effect of longitudinal mixing will be to increase slightly the concentration of ammonia in the effluent."

---

* All references are collected in the bibliography.

Biological oxidation of ammonia consumes oxygen and, by definition in Standard Methods, is included as part of the BOD_5 test. However, much of the ammonia demand may not show up in five days because of inadequate seed bacteria or excessive competition from heterotrophic forms. The BOD_{20} is more realistic in assessing the oxygen demand due to ammonia in municipal effluents. The oxygen demand from ammonia in industrial effluents is best calculated assuming complete nitrification.

$$1) \quad 2NH_3 + 4O_2 \longrightarrow 2HNO_3 + 2H_2O$$

According to this equation, 1 mg of ammonia nitrogen could exert an ultimate BOD of 4.5 mg of oxygen. Well over 60% of the biological oxygen demand that will be exerted in receiving waters by biologically treated municipal effluents will be due to oxidation of ammonia to nitrate by the stream's flora. The BOD bottle is a relatively inefficient system for nitrification in comparison with the attached flora on the beds of the stream; therefore, reliance on the 5-day BOD bottle has shifted the burden of satisfying nitrogenous oxygen demand from the treatment plant to the receiving water.

It would be beneficial if waste treatment plants were required to produce nitrified effluent. Ammonia nitrogen in effluent has several undesirable features:

(1) Ammonia consumes dissolved oxygen in the receiving water;
(2) Ammonia reacts with chlorine to form chloramines which are less effective disinfectants than free chlorine;
(3) Ammonia is toxic to fish life;
(4) Ammonia is corrosive to copper fittings;
(5) Ammonia increases the chlorine demand at waterworks downstream.

A nitrified effluent, free of substantial concentrations of ammonia, offers several advantages:

(1) Nitrates will provide oxygen to sludge beds and prevent the formation of septic odors;

(2) Nitrified effluents are more effectively and efficiently disinfected by chlorine treatment;

(3) A nitrified effluent contains less soluble organic matter than the same effluent before nitrification.

In general, we can depend on conventional biological processes to transform almost all nitrogenous components in wastewater into ammonia and biological sludge. Once this has been accomplished, we can design systems to remove ammonia by air-stripping, or we can proceed to a second biological conversion of the ammonia into nitrates. A nitrified effluent may be acceptable for discharge, but if the nitrate level is too high it can be further treated by biological action to convert the nitrates to nitrogen gas.

Ammonia and nitrate are interchangeable nitrogenous nutrients for green plants and algae, as well as bacteria. Some species may prefer ammonia, and others nitrate, but in general they can be considered interchangeable (Flaigg and Reif, 1954). When algae grown on nitrates decompose they will liberate nitrogen in the form of ammonia.

Nitrogen and Eutrophication

The head of the National Eutrophical Program of the FWPCA has stated (Bartsch, 1970),

> "In many lakes that are in trouble because of eutrophication, the nutrients of prime significance are nitrogen and phosphorus. Phosphorus is found to be critical in terms of extensive production more frequently than nitrogen. In some cases it has been demonstrated through field study and appropriate assays that nitrogen does occupy a critical role. Reasons for pessimism relative to nitrogen control (of eutrophication) are the following:
>
> "(1) Many microorganisms can fix atmospheric nitrogen and make it available. Included are bacteria, some of the blue-green algae which are causes of bloom problems, and actinomycetes.

"(2) Nitrogen can pass through the soil and into the ground water and find its way into surface waters more easily than phosphorus. Ammonia can also find its way into surface water via precipitation, in some locations up to as much as 20 lbs/acre per year.

"Situations where nitrogen control must be used for control of eutrophication include the upper San Francisco Bay, where it has been demonstrated that nitrogen is the critical element. There is some thought that lakes that are young in the aging process are more likely to be nitrogen limiting than lakes that have started down the pathway of eutrophication. Lake Tahoe is an example where nitrogen may or may not be a limiting nutrient. In some bodies of water where phosphorus may be limiting part of the time during the growing season, nitrogen may normally be limiting at other times. It is possible to exercise some guided judgment in the matter of limiting nutrients through use of test procedures like the Provisional Algal Assay Procedure (PAAP, 1969)."

Nitrogenous Oxygen Demand

The Chief of the Engineering Section, Chesapeake Technical Support Laboratory, Middle Atlantic Region, FWQA, has stated in regard to nitrogen removal needs (Jaworski, 1970):

"In the upper Potomac Estuary about one half of the dissolved oxygen sag is due to a nitrogenous demand of organic matter being discharged from wastewater effluents in the Washington metropolitan area. During the low-flow summer months, dissolved oxygen levels of less than 2 mg/l in a 10-mile reach are common. Studies by CTSL, FWQA and Maryland Department of Water Resources have established that the dissolved oxygen deficits in the middle portion of the Patuxent River basin are mainly attributable to the nitrogenous demand of organic matter originating from wastewater discharges.

"To eliminate the dissolved oxygen deficit in the Potomac Estuary and in the Patuxent River, the removal of nitrogenous demand is required to manage the water quality in both areas. The State of Maryland has gone on record as requiring a maximum of 1 mg/l of ammonia in effluents discharging into the Patuxent River. To enhance the water quality of the Potomac River basin, the recent Potomac Enforcement Conference required 85% removal of the present nitrogenous oxygen demand from treated waste discharges in the Washington metropolitan area.

Algal Growth Response

"At the present time, predictive generalizations cannot be made for the response of algae to nutrients for all receiving waters. Different geophysical systems appear to be responsive to different limiting nutrients.

> "In the Potomac Estuary during summer periods, nitrogen appears to be the rate limiting nutrient at the salinity-freshwater interface. Data from the James River Estuary by VIMS also indicate that the rate limiting nutrient is nitrogen. Thus it appears that nitrogen can be a manageable nutrient with respect to the control of eutrophication.
>
> "If a wastewater system is selected that converts all or most of the nitrogen to nitrates, this will aid the immediate oxygen deficit caused by the oxidation of NH_3 to NO_3. Since NO_3 can be readily converted to organic nitrogen and NH_3 by bacteria and algal cells in waters, the potential nitrogenous demand will still be present. Therefore, carbon and phosphorus as well as nitrogen are the important parameters in the control of eutrophication with respect to the elimination of nuisance algal conditions and the enhancement of water quality.
>
> "While the control of organic carbon and phosphorus will reduce the incidence of algal blooms, the addition of nitrogen removal will further enhance the control of the blooms. If wastewater treatment processes are added to convert the nitrogen to NO_3 without considering the complete removal of nitrogen, we are just transporting the problem farther downstream."

The State of Illinois has recently set an effluent standard of 2.5 mg/l of ammonia (2.05 mg/l ammonia-N) for discharge to surface waters. A substantial fraction of the oxygen sag in the Grand and Clinton Rivers in Michigan and in the Kanawha River, West Virginia, below a large industrial complex, has been attributed to the BOD of ammonia. It was early practice in Britain to nitrify effluents as evidence of good biological treatment since nitrification is difficult in the presence of large amounts of readily decomposable organic matter. Furthermore, nitrates in the water provide oxygen to help oxidize organic matter present from other sources, and to prevent septicity. Nitrates, usually as chili saltpeter, have frequently been used to control septic odors in estuaries and lagoons (Lang, 1966).

A review article of British water pollution control (Jenkins, 1970) states that a recent requirement limits ammonia nitrogen in sewage effluents not to exceed 10 mg/l. This means that a treatment plant must be designed to give complete purification to three times the dry weather sewage flow and that 60% to 70% of the ammonia nitrogen must be oxidized at all times. River control agencies regard nitrification as desirable because of the high oxygen demand of ammonia nitrogen, the toxicity of ammonia to fish under certain circumstances, the reduction in chlorine demand, and the oxygen reserve present in nitrates.

Ammonia standards for several states were reviewed by Battelle Northwest (1969).

Ammonia is rapidly adsorbed by soil minerals and particulate matter containing nitrogen is also effectively removed in the soil. However, if there is not sufficient plant growth in the soil to use the bound ammonia, it will be converted to nitrates by nitrifying bacteria. Nitrates are very poorly adsorbed in the soil, and rapidly reach the ground water when present in excess. Therefore, over-fertilization with nitrogen compounds, whether they be ammonia, slow-release nitrogen, or nitrates, can lead to high concentrations of nitrates in ground water.

Ammonia has very little toxicity to humans and there are no limits on ammonia in the USPHS Drinking Water Standards of 1962, or the WHO International Standards. Ammonium compounds have been used in cooking and ammonia gas is the essential ingredient of smelling salts. Various suggested limits on ammonia in drinking water are related to the fact that ammonia is generally taken as an indicator of fecal pollution and the fact that high levels of ammonia dissolve copper from plumbing. The toxicity of ammonia to fish and other aquatic species is much higher than for humans, but details have not been completely elucidated. According to many references, the toxicity of ammonia and ammonium salts to aquatic animals is directly related to the amount of undissociated ammonium hydroxide in the solution, which in turn is a function of pH. Toxicity has been reported at levels as low as 0.2 mg/l of undissociated ammonia nitrogen (McKee and Wolf, 1963).

Nitrates have low toxicity for plants and animals. Saltpeter (potassium nitrate) has traditionally been used as a curing agent for ham. Nitrates in food and water are normally denitrified by bacteria in the intestines. However, some very young babies do not have a complete intestinal flora. The bacteria which are present reduce nitrates to nitrites, and do not carry the reduction further to nitrogen gas. Nitrites combine with hemoglobin to produce methemoglobinemia, a disease characterized by cyanosis. PHS and WHO standards recommend not more than 10 mg/l of nitrate nitrogen (45 mg/l nitrate) for water to be fed to babies. Many well waters contain more than 10 mg/l of nitrate nitrogen, and particularly among poorer classes and migrant laborers it is very difficult to make sure that babies are not given this water.

The following papers discuss specific processes which can be used to remove nitrogen compounds from water.

Paper No. 2

NITROGEN REMOVAL BY BIOLOGICAL SUSPENDED GROWTH REACTORS

E. F. Barth

Other sections of this report deal with chemical and physical processes to remove nitrogenous components of wastewater. While these are being actively investigated, our basic capability resides in carefully managed biological systems. Success in providing a high efficiency for nitrogen removal by biological denitrification requires that the biological transformation of ammonia nitrogen to nitrate nitrogen be under good process control. Any reduced nitrogen compounds introduced into the denitrification stage will pass through the process unaltered and impair overall nitrogen removal efficiency.

Downing and Hopwood (1964) revealed the complex factors involved in maintaining nitrification with a conventional activated sludge system. A three sludge variation of the activated sludge process has been developed which greatly simplifies the process control problems associated with maintaining nitrification (Barth, et al., 1968). Figure 1 is a schematic of the process developed for nitrogen removal by biological denitrification. Figure 2 is a representation of a municipal application of the three sludge system taking advantage of common wall construction techniques for economy in construction.

The three sludge system allows management of the separate biological transformations which are necessary for successful denitrification. As shown on Figure 1 the high rate system handles the bulk of the carbonaceous removal and at this station the waste activated sludge is removed. Thus, the nitrification stage receives a predominantly ammonia nitrogen feed and an enriched culture develops because each system has its own sludge recycle. This process design also has other desirable features. The high rate system protects subsequent nitrification stages from toxic chemicals. Heavy metals, cyanides, thiocyanates, and toxic organic chemicals will be either sorbed or biologically degraded before they reach the nitrification stage. Since this is a staged system there can be no direct short circuiting of materials from the influent to the effluent. Temperature effects on the enriched culture of the nitrification stage are not as extreme as with a single sludge system which contains only a marginal population of nitrifying organisms.

Once controlled nitrification has been established the biological denitrification process can be optimized. The nitrified effluent flows to a stirred anaerobic reactor where methyl alcohol is added in proportion to the nitrate nitrogen concentration. The organisms in this stage use the oxygen component of the nitrate radical to oxidize the organic carbon of methyl alcohol. The end products of this metabolism are elemental inert nitrogen gas and carbon dioxide, which are liberated to the atmosphere.

The stage approach to nitrification has been investigated through grant and contract activities and work at the Robert A. Taft Water Research Laboratory. Large pilot plant operations are located at the University of Notre Dame and Manassas, Virginia. The process has also been evaluated at a 1 MGD scale at Hazel Crest, Illinois. Temperatures as low as 6° C have been recorded, with no detrimental effect on nitrification. Previous experience with the stage approach to nitrification has been reported by English and South African investigators (Osborn, 1965).

Biological denitrification has been studied by microbiologists for many years, particularly in regard to loss of nitrogen from soils (van Schreven, 1963). There have been intensive recent studies related to the application of denitrification to wastewaters. Wuhrman (1960) and Bringmann and Kuhn (1965) have both published in Europe. American experience includes studies at the Robert A. Taft Water Research Laboratory (Barth, et al., 1968); the Lebanon Plant, Firebaugh, California (McCarty, et al., 1969); Notre Dame, Indiana (Echelberger and Tenney, 1969); Manassas, Virginia (Mulbarger, et al., 1969); and Pomona, California (Carey, 1968). A summation of these studies show that biological denitrification is a controllable process if the reaction is forced with an organic supplement, such as methyl alcohol. Attempts to use waste organic matter from sewage have been less successful.

Packed column processes as well as suspended growth reactors have given efficient nitrogen removal. Large scale municipal application, in the range of 2 MGD or greater would favor suspended growth reactors. The 300 MGD Blue Plains Washington, D. C. municipal facility tentatively is being designed on the basis of a three-stage biological system for both nitrogen and phosphorus removal after an extensive review of both chemical-physical approaches and biological approaches to nitrogen removal.

The Blue Plains plant will employ a final filtration step to assure quality control of the effluent. Filtration of effluents is necessary for high efficiency whether we are considering suspended solids, chemical oxygen demand, nitrogen, or phosphorus. We must have positive control of the solids no matter what treatment process we employ.

Figure 2 showing the municipal application of this process indicates that the current technology development of high purity oxygen for carbonaceous removal can be combined with this staged system to give very reasonable detention times. A two hour oxygen aeration period combined with one hour detention in each of the settlers, and two hours each for nitrification and denitrification give a total flow through time of ten hours.

The three-stage biological system can produce an effluent containing 2 mg/l, or less, of total nitrogen. This is a very realistic figure to use as an effluent standard, and when dealing with municipal wastewaters it represents 90 percent or greater removal of total nitrogenous materials.

The capital cost of such a system would be about 25 percent more than a conventionally designed activated sludge process of equal flow. The use of high purity oxygen in the first and second stages could bring the capital cost almost exactly in line with conventional capital costs.

The operating cost for the methyl alcohol to supplement the denitrification process is 1.6 cents per thousand gallons for a wastewater containing 20 mg/l of nitrogenous material.

In order to make more information available than is possible in the above narrative summary, reproductions of the slides used to present this topic, at Dallas, Texas, are attached after Figure 2.

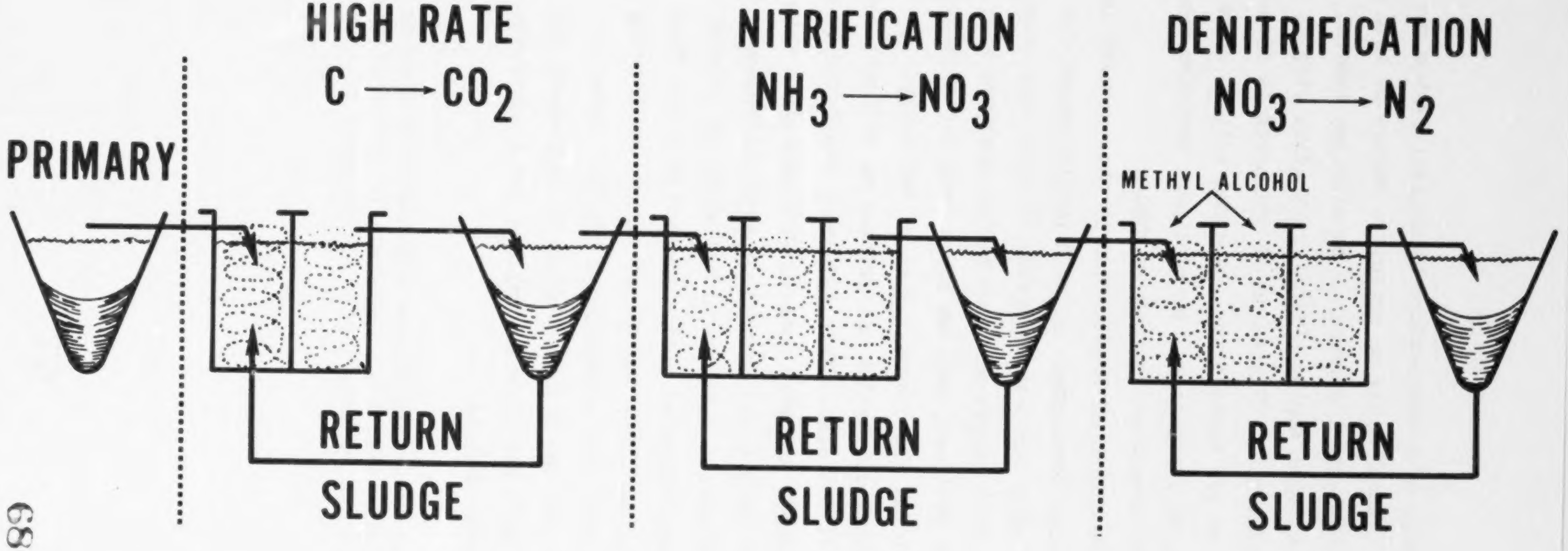

HIGH RATE
$C \longrightarrow CO_2$
NITRIFICATION
$NH_3 \longrightarrow NO_3$
DENITRIFICATION
$NO_3 \longrightarrow N_2$
PRIMARY
METHYL ALCOHOL
RETURN SLUDGE
RETURN SLUDGE
RETURN SLUDGE

FIGURE I

THREE SLUDGE SYSTEM FOR NITROGEN REMOVAL

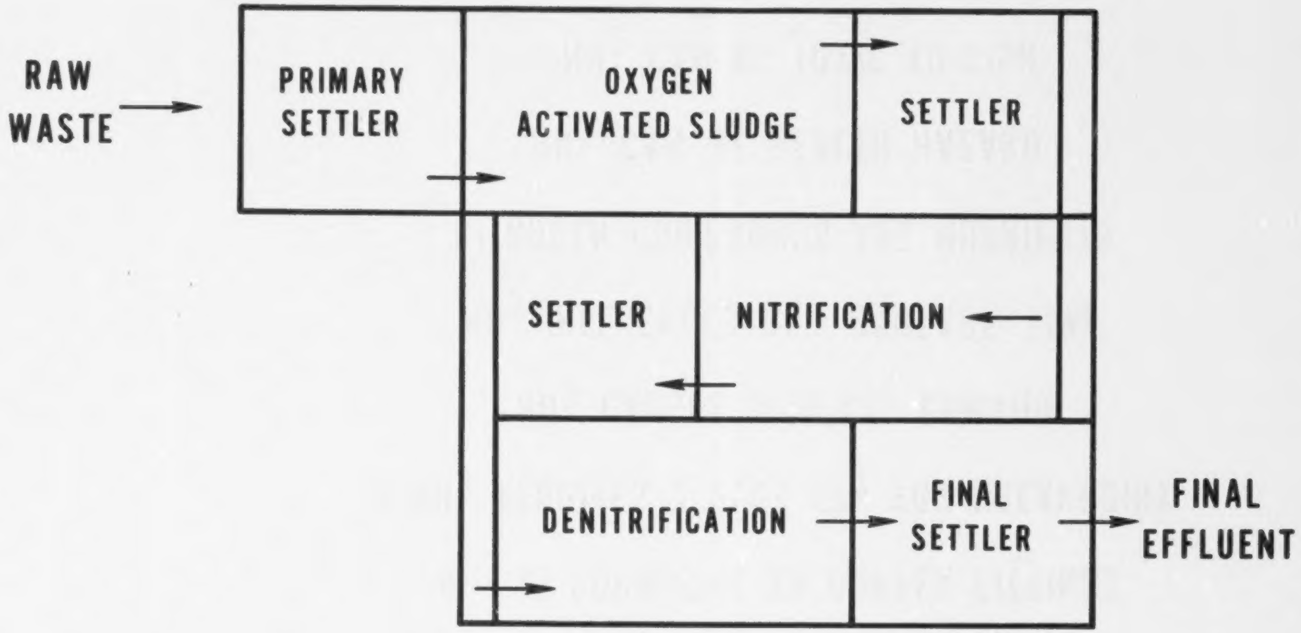

RAW
WASTE
PRIMARY
SETTLER
OXYGEN
ACTIVATED SLUDGE
SETTLER
SETTLER
NITRIFICATION
DENITRIFICATION
FINAL
SETTLER
FINAL
EFFLUENT

FIGURE 2

COMMON WALL CONSTRUCTION OF 3-SLUDGE SYSTEM

TABLE II

IMPORTANCE OF NITROGEN

NH_3 IN EFFLUENTS CAN CAUSE DO SAG IN RECEIVING WATER

NH_3 IS CORROSIVE TO COPPER FITTINGS

1 NH_3 REQUIRES 7 PLUS $C\ell_2$ FOR BREAKPOINT

NO_2 CAUSES HIGH $C\ell_2$ DEMAND

NH_3 INFLUENCES $C\ell_2$ CONTACT TIME

NITROGEN COMPOUNDS ARE NUTRIENTS

NO_3 CAN BE HEALTH HAZARD

NH_3 CAN BE TOXIC TO FISH

TABLE III

RELATIONSHIP OF CARBONACEOUS OXIDATION AND AMMONIA OXIDATION, BEFORE AND AFTER TREATMENT TO REMOVE 90% OF CARBONACEOUS MATERIAL

	mg/l	
	WASTEWATER	FINAL EFFLUENT
ORGANIC MATTER	250	25
ORGANIC OXYGEN DEMAND	375	37
NH_3	25	20
AMMONIA OXYGEN DEMAND	112	90
TOTAL OXYGEN DEMAND	487	127
PERCENT OF OXYGEN DEMAND DUE TO NH_3	22%	71%

TABLE IV

NITROGEN REMOVAL PROCESSES

$$NH_3^\circ \text{ (SOLUTION) } \xrightarrow{\text{air}} NH_3^\circ \uparrow \text{ (GAS)}$$

$$NH_4^+ \longrightarrow \text{CLINOPTILOLITE} \bullet NH_4$$

$$NO_3^- \longrightarrow \text{RESIN} \bullet NO_3$$

REVERSE OSMOSIS

ELECTRODIALYSIS

DISTILLATION

$$2\ NH_3 + 3\ Cl_2 \longrightarrow N_2^\circ \uparrow + 6\ HCl$$

$$NO_3^- + Fe^{++} \xrightarrow{Cu} N_2^\circ \uparrow + Fe^{+++}$$

$$NO_3^- \xrightarrow[\text{organisms}]{\text{organic C}} N_2^\circ \uparrow + CO_2$$

UNIT EFFICIENCIES, PER CENT REMOVAL

Plant	Primary			Secondary			Overall		
	COD	SS	N	COD	SS	N	COD	SS	N
Archbold	43	58	9	89	87	57	94	94	61
Hamilton	55	57	-27	77	86	34	90	94	16
Lebanon	62	65	28	45	55	42	79	84	58
Loveland	0	15	0	61	56	30	61	62	30
Milford	23	55	17	60	61	25	69	82	38

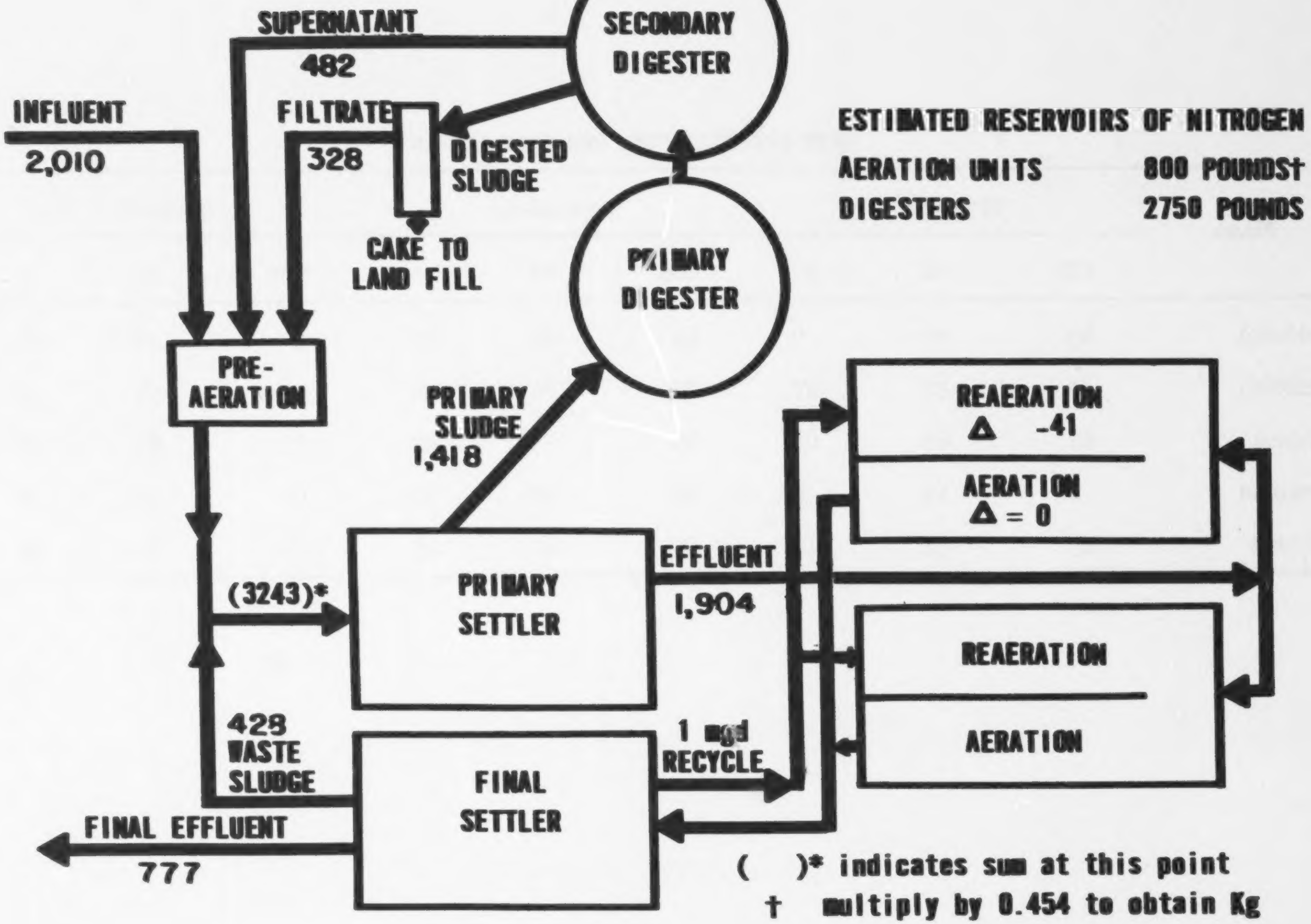
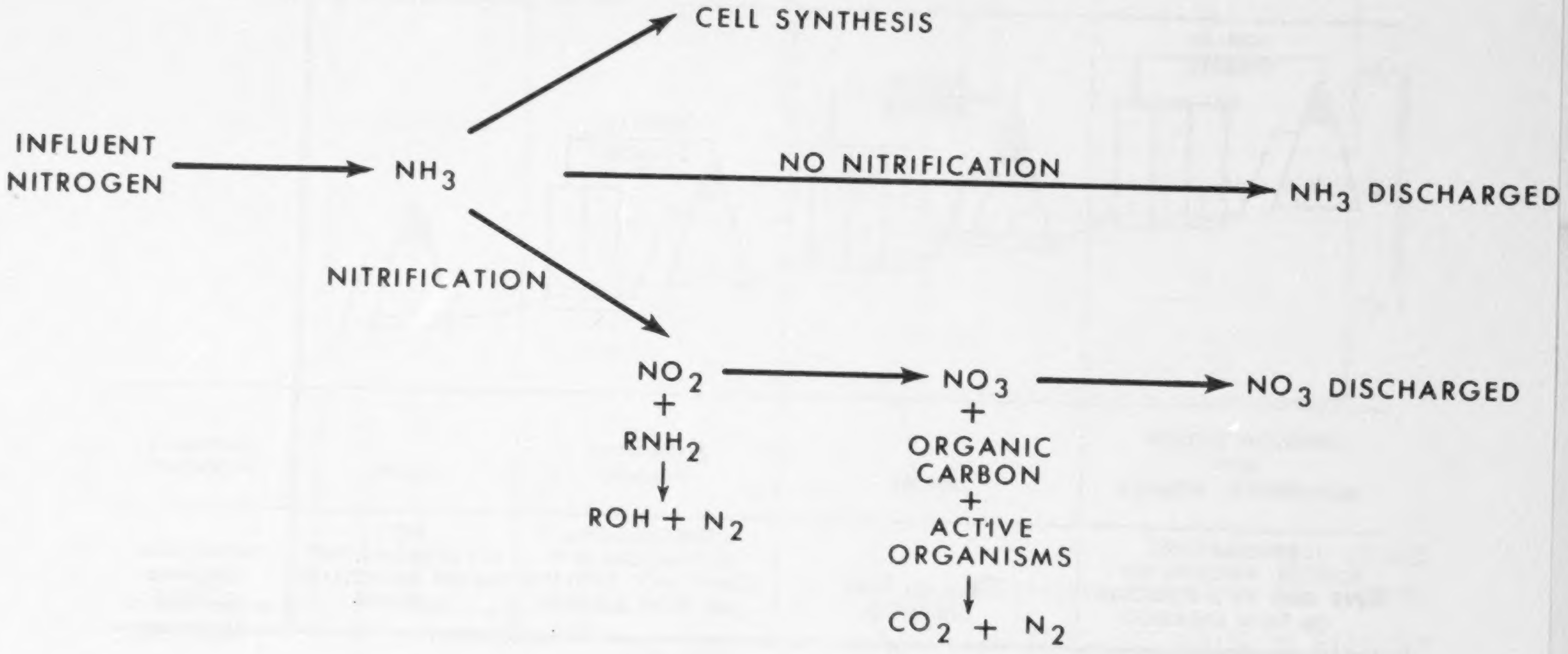

SUPERNATANT
482
SECONDARY DIGESTER
INFLUENT
2,010
FILTRATE
328
DIGESTED SLUDGE
CAKE TO LAND FILL
PRIMARY DIGESTER
ESTIMATED RESERVOIRS OF NITROGEN
AERATION UNITS 800 POUNDS†
DIGESTERS 2750 POUNDS
PRE-AERATION
PRIMARY SLUDGE 1,418
REAERATION Δ -41
AERATION Δ = 0
EFFLUENT
1,904
(3243)*
PRIMARY SETTLER
REAERATION
AERATION
428 WASTE SLUDGE
1 mgd RECYCLE
FINAL SETTLER
FINAL EFFLUENT
777
( )* indicates sum at this point
† multiply by 0.454 to obtain Kg

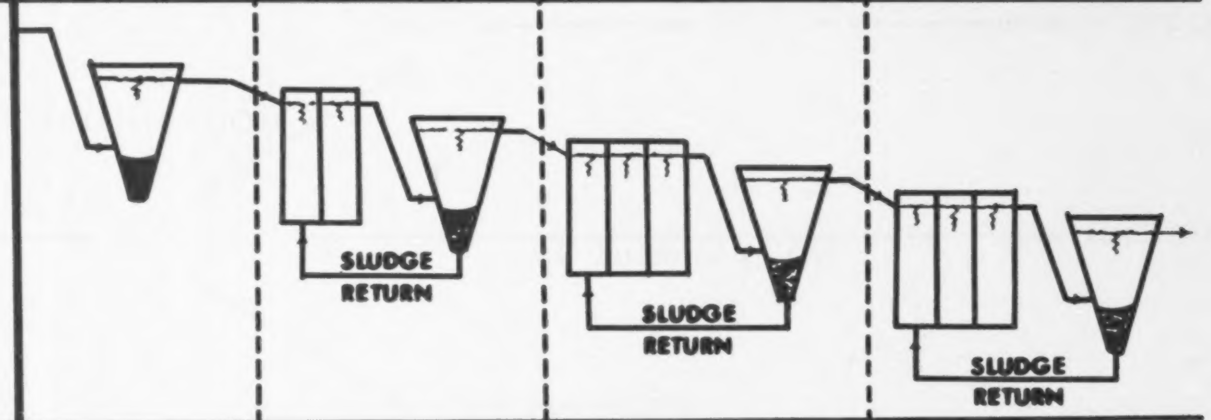
Figure 1. FIVE-DAY NITROGEN BALANCE: ARCHBOLD, OHIO. ALL VALUES IN POUNDS

NITROGEN CYCLE


INFLUENT NITROGEN
NH3
CELL SYNTHESIS
NO NITRIFICATION
NH3 DISCHARGED
NITRIFICATION
NO2 + RNH2 → ROH + N2
NO3 + ORGANIC CARBON + ACTIVE ORGANISMS → CO2 + N2
NO3 DISCHARGED

PROCESS FLOW DIAGRAM

MAJOR PROCESS FUNCTIONS	REMOVE SETTLEABLE SOLIDS AND PARTICULATE COD	REMOVE BULK OF SOLUBLE ORGANICS AND PRECIPITATE PHOSPHORUS	CONVERT NH_3 TO NO_3	CONVERT NO_3 TO NITROGEN GAS AND CO_2 AND FURTHER REDUCE PHOSPHORUS
CHEMICAL ADDITIVES	NONE	SODIUM ALUMINATE	NONE	SODIUM ALUMINATE AND METHYL ALCOHOL
Unit	Primary	High—Rate	Nitrification	Denitrification


SLUDGE RETURN
SLUDGE RETURN
SLUDGE RETURN

MIXED LIQUOR CHARACTERISTICS AFTER ADDITION OF ALUMINUM

	Sludge Age days (Approx.)	MLSS mg/1	MLVSS mg/1	% Volatile	SDI	% Nitrogen V. S. Basis	% Phosphorus V. S. Basis	% Aluminum V. S. Basis
High-Rate Mixed Liquor	2	3, 385	1, 740	51	1. 12	8. 3	12. 3	11. 0
Nitrification Mixed Liquor	22	1, 195	770	64	1. 15	10. 6	8. 0	6. 6
Denitrification Mixed Liquor	38	2, 010	1, 385	69	1. 46	9. 7	8. 7	6. 0

TABLE IV - Change in Concentration of Various Constituents During Treatment *

Constituent	Raw waste-water mg/l	Primary effluent mg/l	High-rate effluent mg/l	Nitrified effluent mg/l	Denitrified effluent mg/l	Denitrified effluent (filtered) mg/l
COD						
Average	320	218	64	43	44	38
Range	95-1,195	67-566	24-328	17-239	21-194	15-194
Organic-N						
Average	10.3	5.9	0.8	0.4	0.4	0.2
Range	2.3-31	1.4-12	0.8-1.4	0.0-1.0	0.0-1.7	0.0-1.6
Ammonia-N						
Average	11.3	13.7	7.7	0.6	0.3	0.4
Range	0.2-24	2.5-21	0.2-16	0.0-6.0	0.0-2.2	0.0-2.3
Nitrite-N						
Average	--	--	1.1	0.3	0.3	0.4
Range	--	--	0.0-5.8	0.0-2.6	0.0-1.8	0.0-1.9
Nitrate-N						
Average	--	--	4.3	11.5	0.9	0.9
Range	--	--	0.0-10.5	3.7-24.8	0.0-7.5	0.0-6.1
Total phosphorus						
Average	12.6	11.9	2.8	2.6	1.5	1.1
Range	3.0-30	3.0-26	0.4-11.3	0.7-8.2	0.2-5.3	0.2-4.5
S.S.						
Average	157	90	8.8	7.1	7.1	1.7
Range	40-800	28-236	0.0-39	0.0-54	0.0-45	0.0-7
pH						
Mode	7.2	7.3	7.5	7.5	7.7	7.7
Range	6.7-7.6	6.9-7.6	7.2-7.8	7.1-8.0	7.2-8.0	7.0-8.3

---

* Each average is result of 40 determinations.

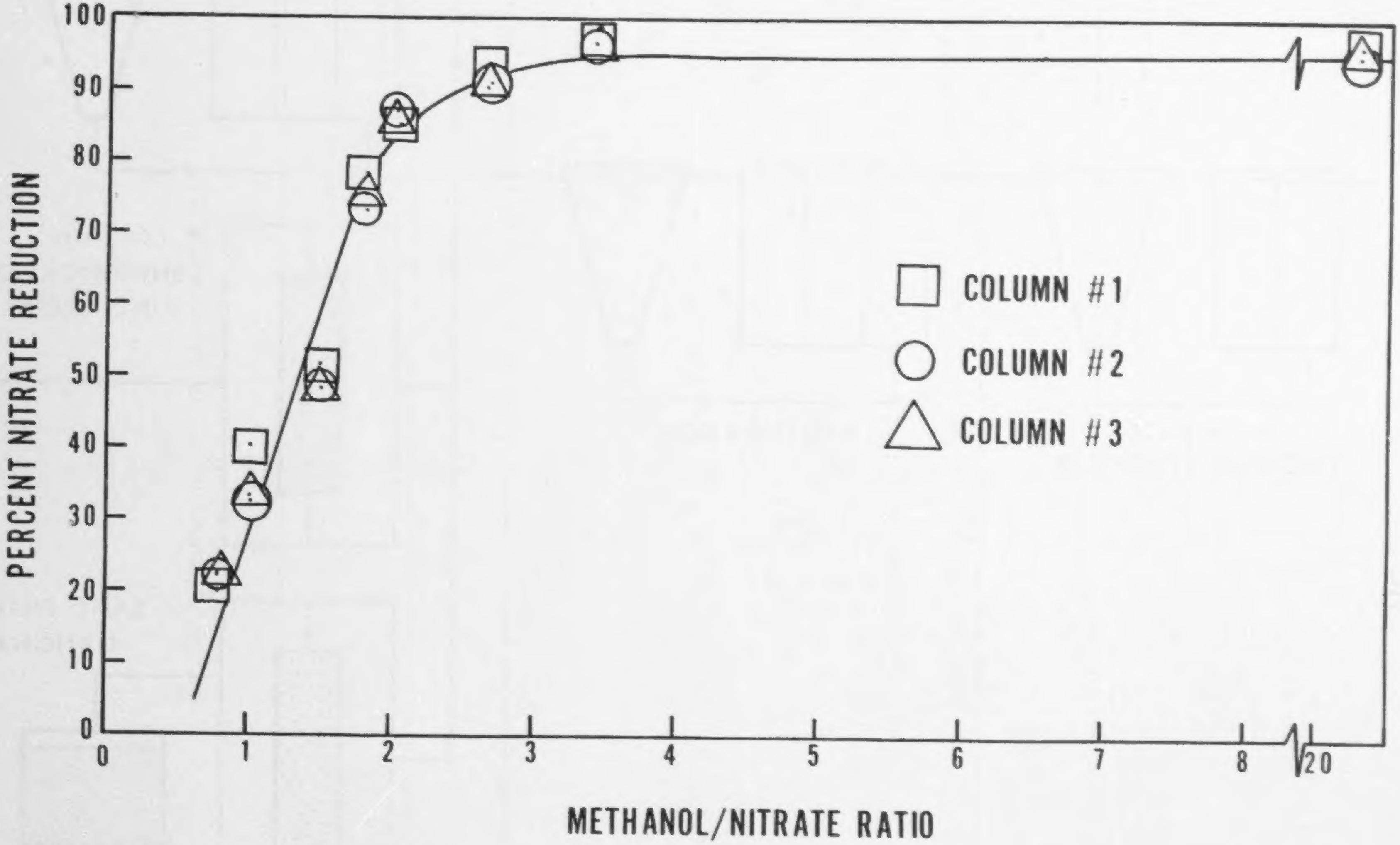


FIGURE 8

PERCENT NITRATE REDUCTION vs. METHANOL/NITRATE RATIO, RUN NO. 1

MODIFICATIONS OF THE DENITRIFICATION PROCESS

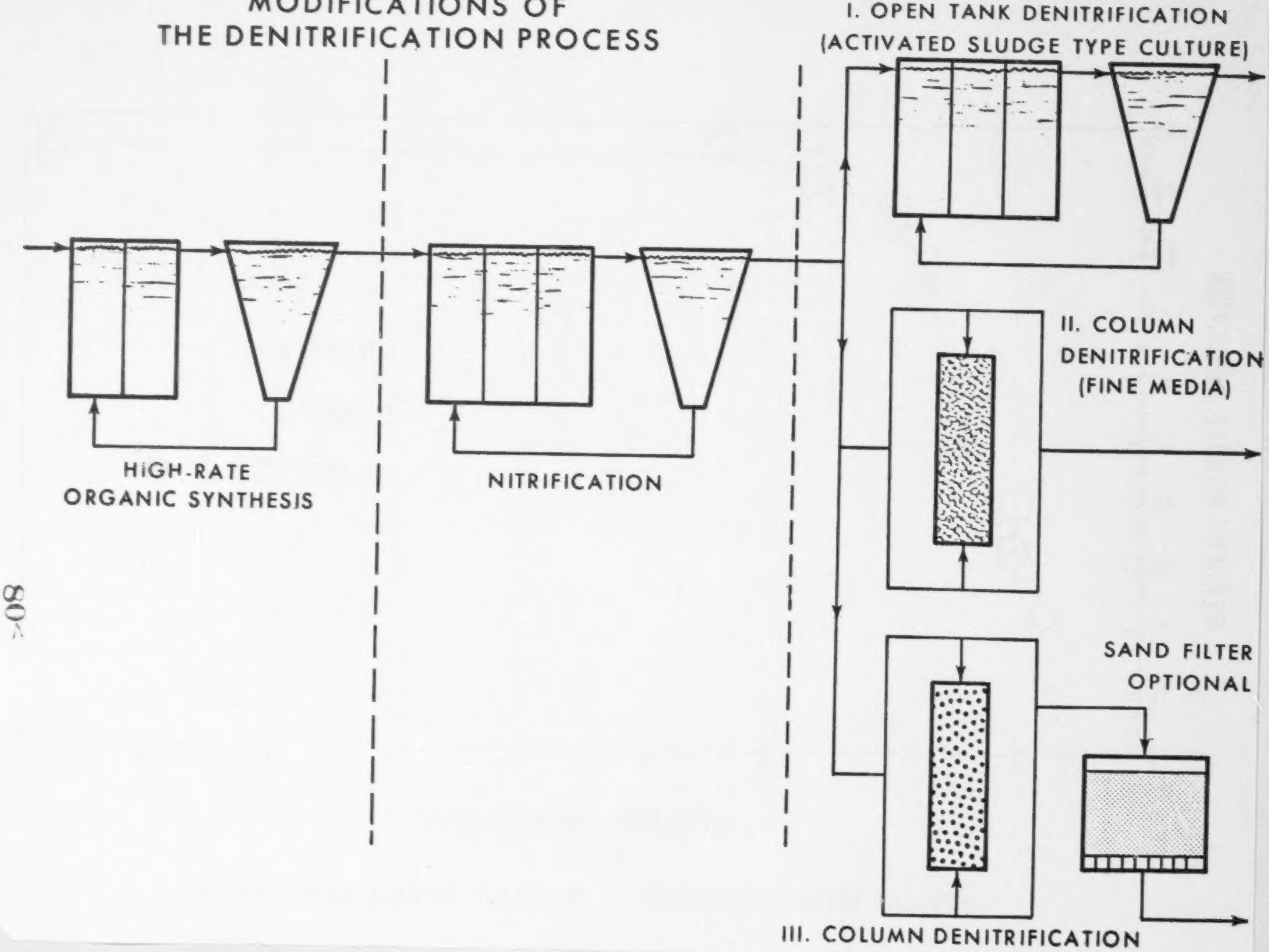
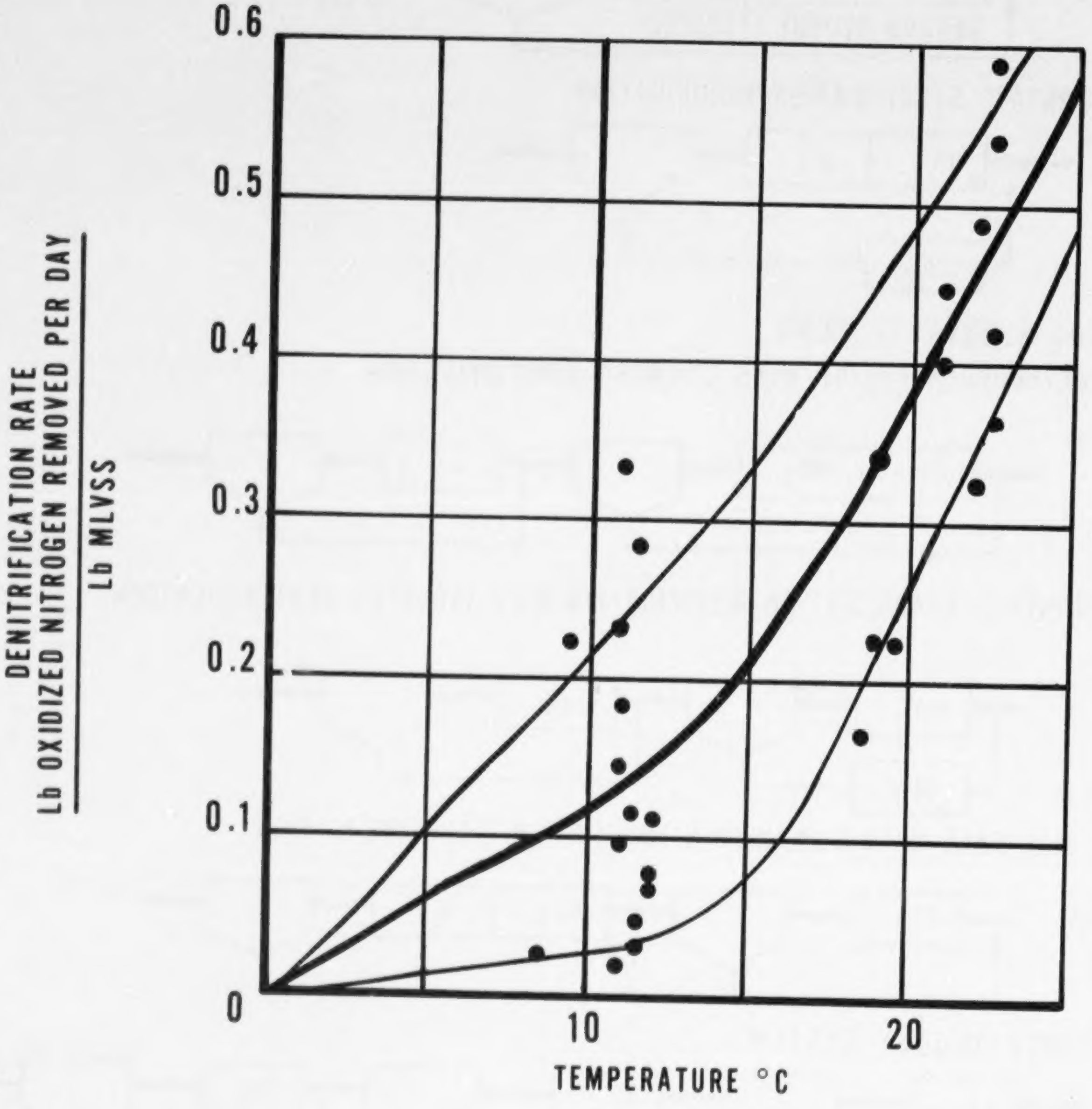

I. OPEN TANK DENITRIFICATION
(ACTIVATED SLUDGE TYPE CULTURE)
HIGH-RATE
ORGANIC SYNTHESIS
NITRIFICATION
II. COLUMN
DENITRIFICATION
(FINE MEDIA)
SAND FILTER
OPTIONAL
III. COLUMN DENITRIFICATION

FIGURE 7 · DENITRIFICATION RATE VS. TEMPERATURE



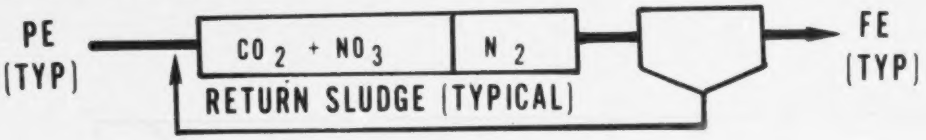
Reference: M. Mulbarger

FIGURE 1

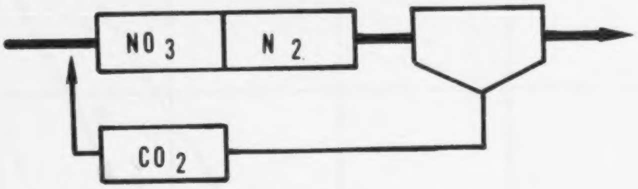
PROCESS ALTERNATIVES FOR NITRIFICATION - DENITRIFICATION

I. SINGLE SLUDGE SYSTEMS

A. EXTENDED AERATION

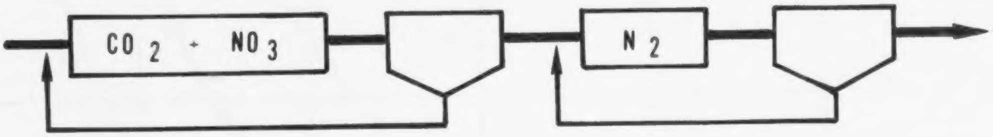

PE
(TYP)
$CO_2 + NO_3$
N_2
RETURN SLUDGE (TYPICAL)
FE
(TYP)

B. CONTACT STABILIZATION MODIFICATION

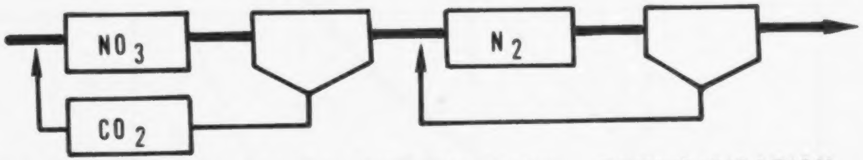


II. DUAL SLUDGE SYSTEMS

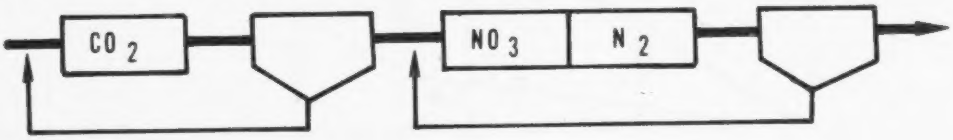
A. EXTENDED AERATION WITH ISOLATED DENITRIFICATION



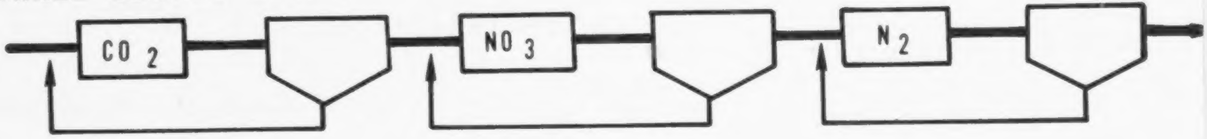
B. CONTACT STABILIZATION MODIFICATION WITH ISOLATED DENITRIFICATION



C. HIGH RATE WITH COMBINED NITRIFICATION - DENITRIFICATION



III. THREE SLUDGE SYSTEM



CODE

CO_2 CARBON REMOVAL (OXIDATION + SYNTHESIS)

NO_3 NITRIFICATION

N_2 - DENITRIFICATION

Reference: M. Mulbarge

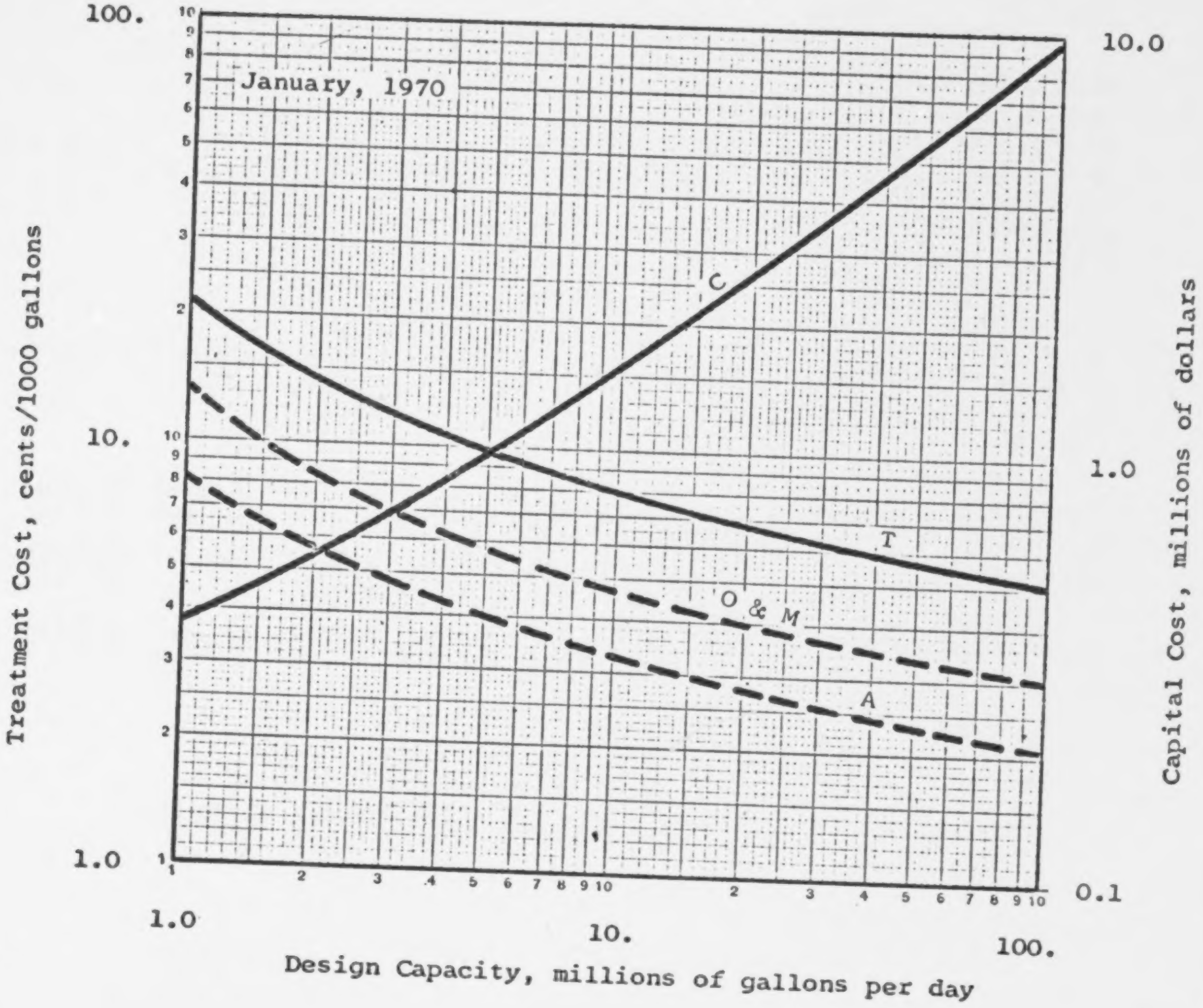
Capital Cost - 10 mgd Plant - Millions of Dollars
(1969-1970 Dollars)

System Item	Standard Activated Sludge	IA	IB	IIA	IIB	IIC	III
Pre-Treatment Control Bldg. primary and final clarification, and disinfection.	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Sludge Thickening, dewatering, treatment and disposal.	2.6	2.2	2.2	2.2	2.2	3.0	3.0
Aeration	$\frac{1.1\ 1.4}{5.2\ 5.5}$					$\frac{0.3\ 0.5}{4.8\ 5.0}$	$\frac{0.3\ 0.5}{4.8\ 5.0}$
Nitrification		1.9 2.7	1.1 1.5	$\frac{1.9\ 2.7}{5.6\ 6.4}$	$\frac{1.1\ 1.5}{4.8\ 5.2}$	0.9 1.1	$\frac{0.9\ 1.1}{5.7\ 6.1}$
Denitrification		$\frac{0.5\ 0.7}{6.1\ 7.1}$	$\frac{0.5\ 0.7}{5.3\ 5.9}$	$\frac{0.9\ 1.1}{6.5\ 7.5}$	$\frac{0.9\ 1.1}{5.7\ 6.3}$	$\frac{0.5\ 0.7}{6.2\ 6.8}$	$\frac{0.9\ 1.1}{6.6\ 7.2}$

Reference: M. Mulbarger

NITRIFICATION AND DENITRIFICATION IN DISPERSED GROWTH REACTORS

Capital Cost, Operating & Maintenance Cost, Debt Service
versus
Design Capacity



C = Capital Cost, millions of dollars
A = Debt Service, cents per 1000 gallons (6% and 25 yr.)
O & M = Operating and Maintenance Cost, cents per 1000 gallons
T = Total Treatment Cost, cents per 1000 gallons

Robert Smith
4676 Columbia Parkway
Cincinnati, Ohio 45226

Paper No. 3

NITROGEN REMOVAL FROM WASTEWATERS BY COLUMN REACTORS

J. M. Smith

Once nitrates are formed in sewage treatment they can be converted to nitrogen gas by the action of microbes and a source of BOD. Columnar nitrate reduction represents an alternate to the suspended growth systems as a means of biochemically reducing the nitrate ion to elemental nitrogen (see Figure 3). A variety of facultative bacteria common in wastewater including the genera *Pseudomonas*, *Achromobacter* and *Bacillus* are known denitrifiers. When supplied with a suitable organic carbon source under anaerobic or near anaerobic conditions these organisms use nitrates and nitrites as the terminal hydrogen acceptors during the fermentation of the added substrate to ultimately form nitrogen gas.

In a packed column the cell residence time of the surface bound slime is much greater than the hydraulic detention time. This, combined with a large contact surface and short diffusion distances afforded by small media such as sand, provides an efficient system for rapid denitrification of an applied feed.

Work at Lebanon, Ohio (J. M. Smith, 1970, Unpublished) has shown that the smaller media systems (sand to 3/4 inch diameter stone) are effective when operated downflow at surface loading rates of 7.0 gpm/ft^2 and at actual contact times of 5 to 30 minutes. The downflow operation, using either granular carbon or sand, requires daily backwashing using 1-3 percent of the throughput stream to relieve pressure drop due to the accumulation of suspended solids in the upper portion of the column. The denitrifying slime is firmly attached to the media surface, and is not removed during the backwash operation. Greater than 90 percent nitrate reduction can be achieved within these columns at contact times of 10 minutes for sand and 30 minutes for the 3/4 inch stone. The effluent normally contains less than 2.0 mg/l of nitrate nitrogen with effluent turbidities less than 3 JTU, indicating little solids contribution from the attached organisms. The ammonia and organic nitrogen content of the feed is not significantly changed during the denitrification process.

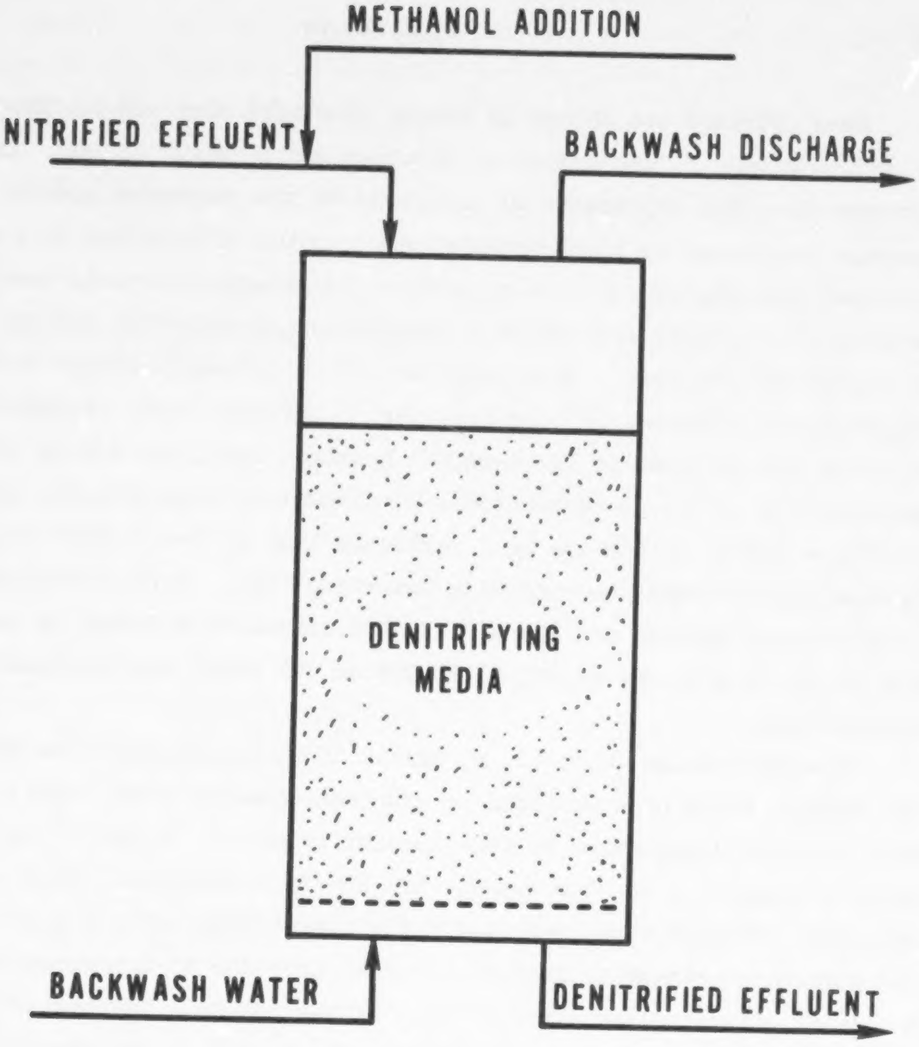

METHANOL ADDITION
NITRIFIED EFFLUENT
BACKWASH DISCHARGE
DENITRIFYING MEDIA
BACKWASH WATER
DENITRIFIED EFFLUENT

FIGURE 3

PACKED BED DENITRIFICATION REACTOR

Larger media varying in size from 1 inch to 2 inch aggregate has been successfully employed to denitrify agriculture subsurface drainage (Tamblyn and Sword, 1969). The larger media permits upflow operation without backwashing at the expense of longer contact times and increased effluent suspended solids. Nitrate reduction of greater than 90 percent can be achieved in contact times of 1 hour for the 1 inch aggregate and 2 hours for the 2 inch aggregate at temperatures above 12° C. The 2 inch columns have been operated continuously for over six months on agriculture subsurface drainage without the loss of efficiency or solids accumulation.

Methanol is used as the supplemental organic carbon source of choice for denitrification because of its low cost, biodegradability and ease of handling. Approximately 3 mg of methanol are required per mg of NO_3-N removed including the requirement for deoxygenating the nitrified feed. The chemical cost for removing 20 mg/l of NO_3-N in the presence of 5 mg/l of dissolved oxygen is estimated to be 1.6¢/1000 gal.

While the packed bed provides an efficient contacting system for denitrification, total nitrogen removal via biological nitrification-denitrification will depend on the combined efficiency of the nitrification stage as well as the denitrification stage. This interdependence of two biological systems will limit total nitrogen removal efficiencies to a practical value of about 90 percent.

Pilot plant experiences to date firmly support a full scale demonstration of columnar nitrate reduction at the 1 MGD level or above. One possibility is the construction of a new facility that incorporates a two stage nitrifying system followed by columnar denitrification. An alternate, and equally plausible idea is to modify an existing conventional activated sludge process by splitting the aeration tanks into a two sludge system by the addition of a second settler, perhaps a tube settler, followed by denitrification on a relatively fine media that will also serve as a solids polishing process. The design of a denitrification system is straightforward and involves basic principles of biological oxidation and filtration. When furnished with basic denitrification data any competent sanitary engineering firm should be able to successfully design a treatment plant capable of removing nitrogen.

St. Armant and McCarty (1969) have demonstrated the use of anaerobic filters for removal of nitrates from irrigation return flow collected in drain tiles. They found that methanol requirements were close to the theoretical. The most satisfactory media was one inch diameter gravel operated upflow. Detention times of one hour were satisfactory at temperatures above 12°C. The treated water contained less than 1 mg/l nitrate and slightly more nitrite. It had no dissolved oxygen. Sludge production by the denitrifying organisms produced turbidity which would have to be removed by filtration.

Paper No. 4

AMMONIA NITROGEN REMOVAL BY STRIPPING WITH AIR

J. B. Farrell

Ammonia is a gas which dissolves in water to an extent controlled by the partial pressure of the ammonia above the water. An increase in its partial pressure causes more ammonia to dissolve, reducing its partial pressure causes ammonia to leave the water phase and enter the gas phase. If it is desired to remove ammonia from water, this can be done by contacting the water with a sufficient quantity of ammonia-free air. This physical process is called desorption or, more commonly, "stripping."

Wastewater contains the ammonium ion at concentrations which typically range from 15 to 25 mg/l. If the ammonium ion is converted to dissolved ammonia by raising the pH, the ammonia may be stripped out by contacting the wastewater with air. Early studies of feasibility of stripping of ammonia from wastewater (Kuhn, 1956) showed a major difficulty: the volume of air per unit volume of water is very high, about 400 cubic feet per gallon of water in a countercurrent-flow packed tower. The pressure drop across a packed tower is about 1.0 psi or 28" of water. Since power is proportional to the product of volumetric flow rate and pressure drop, the cost for power made the process prohibitive even at this relatively low pressure drop.

The problem of high power cost was solved by investigators at the South Lake Tahoe Public Utility District (Slechta and Culp, 1967) who used a slat-filled tower such as is used for cooling water to contact water and air. The pressure drop across such a device is very low--about 1/2 inch of water--so power costs are reduced to reasonable levels. Removal efficiencies as high as 90 percent were obtained in a 24-foot high tower in which water and gas were contacted in a nearly countercurrent fashion. On the basis of this experience, a full scale stripping tower was constructed at South Lake Tahoe. The tower was designed to remove 90 percent of the ammonia from 3-1/2 MGD of Tahoe's renovated wastewater. The air flow is not countercurrent to the water but flows across the tower (cross-flow), while the water drips downward through the packing.

Initial operation of Tahoe's stripping tower was in the winter and immediately revealed a limitation of ammonia stripping. The cold air contacting the wastewater quickly cooled the water. Ammonia solubility is higher in cold water than in warmer water; consequently, more air is required to remove it. For example, at 0° C it would take about 800 cubic feet of air per gallon of water to remove 90 percent of the ammonia from wastewater in a countercurrent tower. Since the Tahoe tower was designed for 400 cubic feet per gallon, percent removal was much lower than 90 percent. When air temperature fell below 0°, freezing of water occurred at the air inlets, making the tower inoperable. From theoretical considerations, difficulty with freezing may be anticipated when the wet-bulb temperature of the ambient air is below 0° C.

Another problem which developed at Tahoe is the formation of scale in the tower. The scale is chiefly calcium carbonate. It forms because the previously lime-treated effluent is supersaturated with respect to calcium carbonate. A more important reason is the presence of carbon dioxide in the air. A small portion of the carbon dioxide reacts with the basic wastewater, forming calcium carbonate which precipitates. In the case of the tower at Tahoe, the sludge can be flushed from the tower except from inaccessible areas which cannot be reached with a water jet. A pilot plant ammonia stripping tower at Blue Plains, Washington, D. C., had similar scaling problems, except the scale is hard and adheres to the tower fill. They have been able to get a soft scale by reducing the pH to 10. A pilot tower in New England had similar hard scale (Sawyer, 1970). However, a pilot plant tower has been run in South Africa (van Vuuren, 1970), and here the scale has been so soft that the force of the water dripping through the tower fill has been sufficient to flush out the scale.

The causes of the differences in the nature and amount of scale in various locations has not been resolved. Some suggested factors influencing the nature of the scale are: type of contact (countercurrent or cross-flow), recirculation of sludge, pH of the wastewater, and chemical makeup of the wastewater. Studies are in progress to see if the scale can be prevented from forming, or if it can be made nonadherent.

The cost of ammonia stripping has been estimated by Suhr (1969) for South Lake Tahoe facility to be about 2.9¢ per 1000 gallons of wastewater treated. This does not include the cost of the lime and facilities to raise the pH to about 11. These costs have been charged to phosphorus removal because this is the direct objective of the lime addition. If 90% removal of ammonia nitrogen is required even in cold weather, these costs should be increased by about 50% to provide for a higher air-to-water ratio. In below-freezing weather the tower will be inoperable. It is possible to heat the incoming air to temperatures above 0° C and add moisture to it to prevent freezing. This procedure would only be economical if subfreezing days are rarely encountered.

Methods for designing ammonia stripping towers have been developed at the Taft Center by Roesler et al. (1970) but have not yet appeared in the literature. Ammonia stripping is feasible when the temperature is above freezing but there is danger of serious fouling by scale. The best approach for minimizing scale and its effects appears to be to use a pH of about 10.5, countercurrent operation rather than cross-flow, and an open fill to allow for easy flushing of accumulated solids.

In order to make more information available than is presented in the above summary, reproductions of some of the slides used in the oral presentation given at Dallas, Texas have been attached.

VAPOR PRESSURE OF A GAS DISSOLVED IN WATER

Henry's Law

At low concentrations, Henry's Law holds:

$$\text{Vapor Pressure of Dissolved Substance} = H \cdot \text{Concentration of Dissolved Substance}$$

Alternative Forms:

$p_a = H \cdot c_a$ where p_a = vapor pressure

c_a = concentration

H depends on temperature

$y = k \cdot x$ where y and x are mol fractions of A in vapor and liquid

k depends on temperature and atmospheric pressure

COMPARISON OF SOLUBILITY OF CARBON DIOXIDE AND NH_3 IN WATER

TEMPERATURE	HENRY'S LAW CONSTANT (H)	
(°C)	CO_2	NH_3
20	1,420	0.7
40	2,330	1.8
60	3,410	3.8

WHERE $p_a = Hx_a$

p_a = VAPOR PRESSURE OF DISSOLVED SUBSTANCE "a" (atm)

x = MOLE FRACTION OF "a"

H = HENRY'S LAW CONSTANT

MINIMUM AIR REQUIREMENT FOR STRIPPING NH3 AND CO_2 FROM WATER AT 20°C IN A COUNTERCURRENT OPERATION

Stripping NH_3 out of basic solution*		Stripping CO_2 out of acidic solution*	
NH_3 in water	NH_3 in air	CO_2 in Water	CO_2 in air
20 mg/l	↑ 8.7×10^{-6} g/g	20 mg/l	↑ 17.6×10^{-3} g/g
2 mg/l ↓	0	2 mg/l ↓	0

Air Required: 225 cu ft/gal 0.11 cu ft/gal

*Entering water stream and exiting air stream are assumed to be in equilibrium

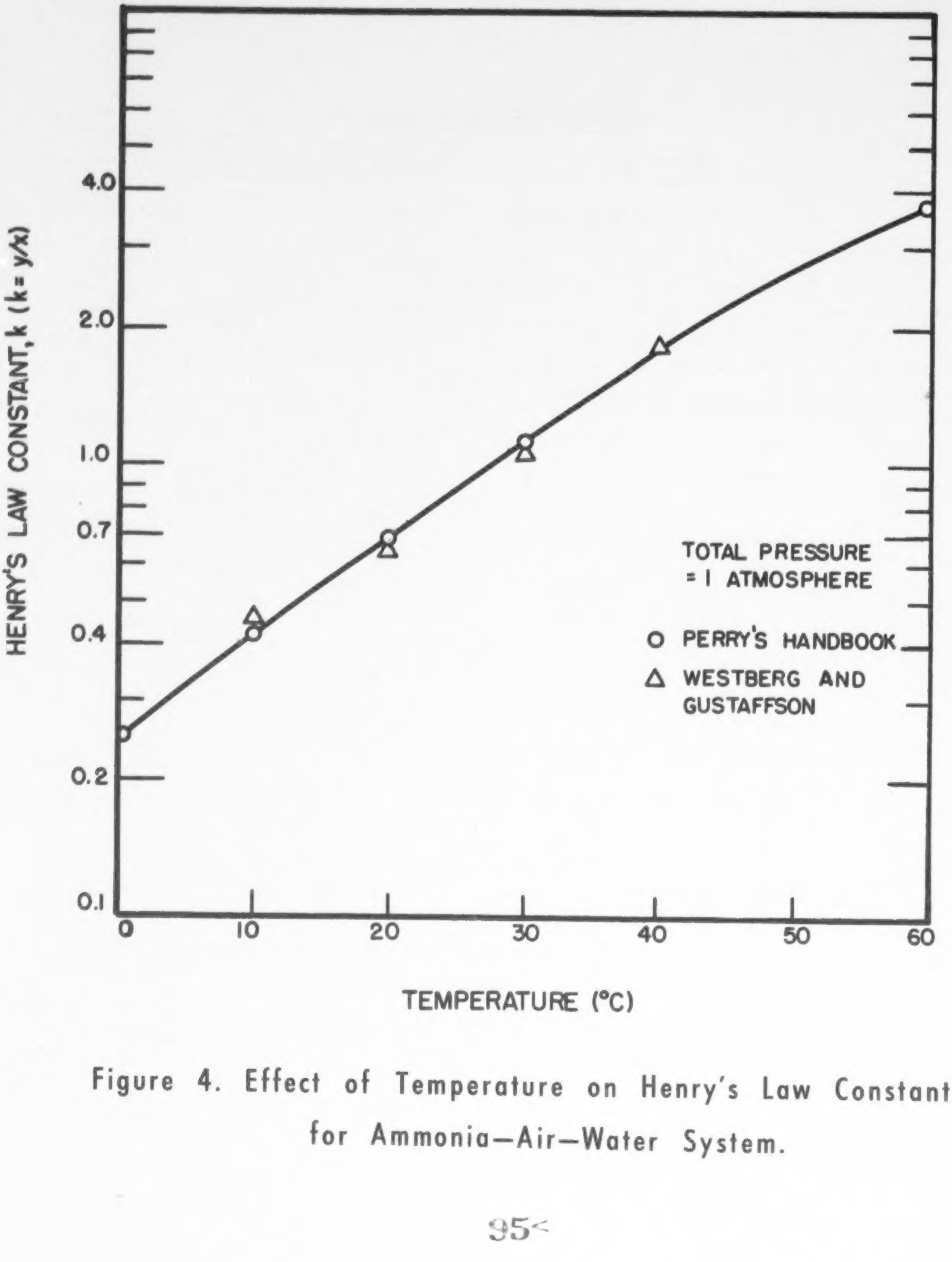


Figure 4. Effect of Temperature on Henry's Law Constant for Ammonia–Air–Water System.

Paper No. 5

REMOVAL OF AMMONIA NITROGEN BY SELECTIVE ION EXCHANGE

R. B. Dean

Ammonia exists in solution predominantly as the ammonium cation (NH_4^+) unless the pH is higher than about 9.5. The ammonium ion is very similar to the potassium ion in size and is precipitated by the same reagents that precipitate potassium. Adsorption of ammonium ion on ion exchange resins is ordinarily very similar to the adsorption of potassium or sodium ions. Therefore, conventional water softening ion exchange resins which are selective for calcium and magnesium do a relatively poor job of removing ammonium from dilute solutions. Total deionization by mixed bed ion exchange resins will, of course, remove ammonium ions along with other cations but this process is too costly for wastewater treatment.

Certain zeolites show unusual selectivity for the ammonium ion. A number of these have been investigated by the Atomic Energy Commission because they also show selectivity for cesium and potassium ions. A demonstration project at the Battelle Memorial Institute - Pacific Northwest (Hanford) Laboratories, 1969 (see Mercer, 1970), showed that certain zeolites, including the naturally occuring mineral clinoptilolite, had a high selectivity for ammonium in natural and wastewaters. A trailer mounted demonstration plant with a capacity of 100,000 gallons per day was built as a cooperative demonstration project between the FWQA and Battelle-Northwest. This trailer is now operated under contract to the FWQA to demonstrate selective ion exchange removal of ammonium ions from solution.

Preliminary work demonstrated that native clinoptilolite from Hector, California, could be used after grinding and sieving to 20 x 50 mesh. When columns filled with this material were fed secondary effluent they clogged rapidly; therefore, the trailer incorporates an inclined-tube settler clarifier to remove turbidity from the feed. Clarified water is treated by conventional downflow through two columns in series. When ammonia breaks through the second column, the first column is taken offstream and a third column containing freshly regenerated clinoptilolite is added after the second column which now becomes the first in the series. The loaded column is regenerated by backwashing with limewater containing sodium chloride to speed up the rate of regeneration. The concentration of sodium chloride is approximately that which will be reached after several regeneration cycles. The high pH of the limewater converts the ammonium ion to unionized ammonia gas in solution. This is allowed to build up to a level of about 500 mg/l by recycling of the limewater. Precipitates such as magnesium hydroxide which may form in some hard waters are removed by settling.

The ammonia laden limewater is then pumped through a packed column through which heated air is blown to remove the ammonia. The problems of ammonia dispersal to the atmosphere are similar to those encountered in direct air stripping of ammonia. However, the ammonia content of the gas stream is 20 to 50 times as strong as occurs with direct air stripping and there is proportionately much less air to be heated in cold weather. On a large scale it would probably be more economical to use stripping towers of the cooling tower type rather than packed towers because the latter have very high pressure drops. However, a packed tower is much more compact and could be incorporated in the available space on the trailer.

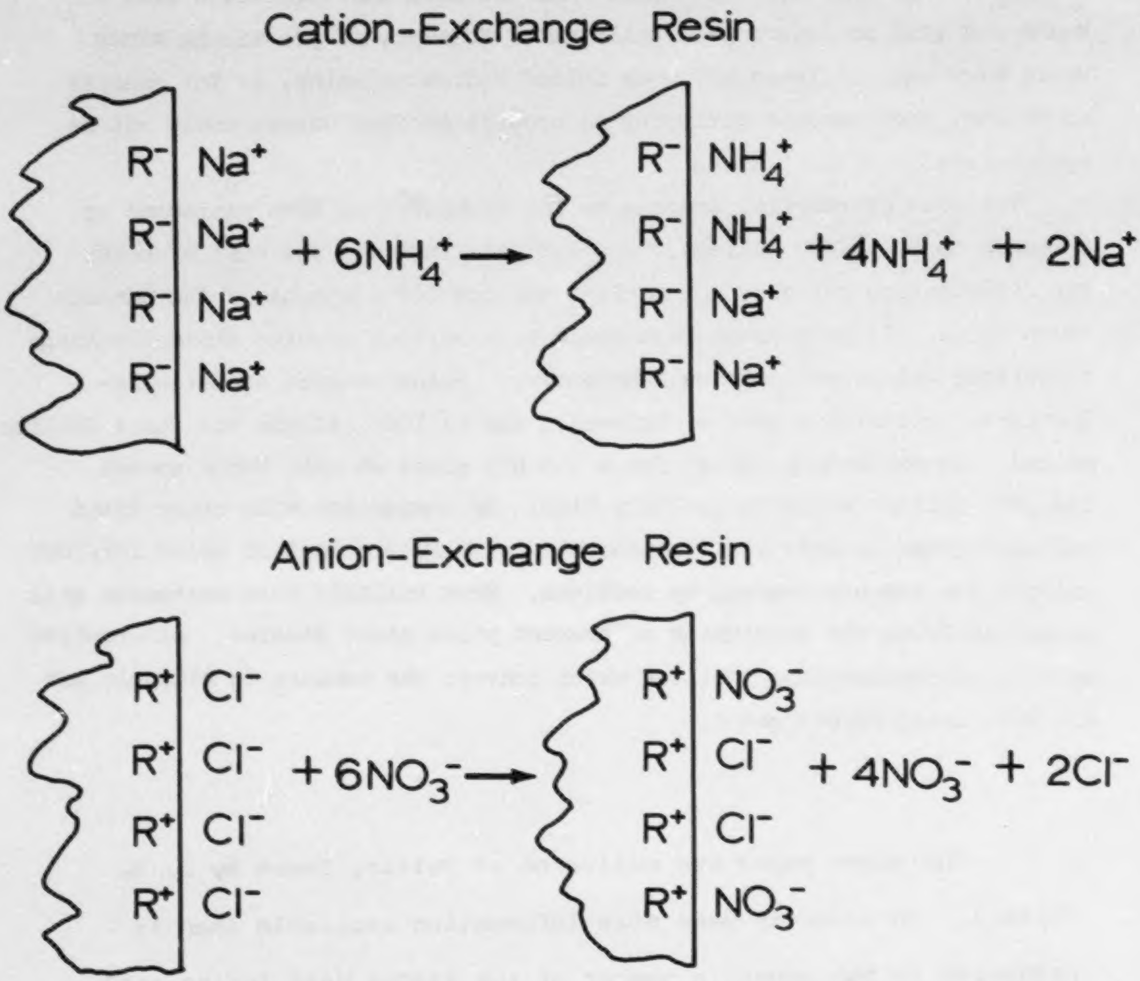
Because of the high concentration of ammonia, its odor is readily detectable in the effluent gases. Of course, the total amount of ammonia vented to the atmosphere is the same whether ammonia is stripped directly or is first concentrated in an ion exchange column. Direct stripping of ammonia from municipal effluents would produce a concentration of ammonia nitrogen in the air of approximately 0.03 ppm, which is well below the threshold for detection by odor.

Ammonia in the atmosphere reacts with sulfur dioxide which is present in large excess over all cities. If all of the ammonia present in sewage in the United States were to be discharged to the atmosphere, it would be equivalent to less than 10 percent of the sulfur dioxide being discharged to the atmosphere. Ammonia and SO_2 together can cause fog under some conditions; however, unneutralized sulfur dioxide eventually forms sulfuric acid which is even more objectionable. Further studies on the behavior of ammonia in urban atmospheres are warranted (Miner, 1969).

Ammonia gas in the atmosphere, whether or not it reacts with sulfur oxides, is adsorbed by moisture in soil, vegetation, and open water surfaces. That portion which goes into the soil and vegetation will be bound and will no longer be a pollutant. However, if prevailing winds would blow ammonia laden air over inland bodies of water, as for example at Toledo, then ammonia stripping to protect surface waters would not be appropriate.

The cost of removing ammonia by ion exchange has been estimated by Eliassen as 8.1¢/1000 gallons. His estimate includes the cost of brine for regeneration but does not include the cost of disposal of the ammonia laden brine. In most areas this could be a serious problem since discharge to surface waters would be self-defeating. Pilot studies at Battelle-Northwest indicated a cost of between 3 and 6¢/1000 gallons for their Zeolite method. An estimate prepared for a 7.5 MGD plant at Lake Tahoe showed 15¢/1000 gallons which is probably high. By comparison with other fixed bed adsorption methods it is reasonable to suggest a cost of about 10¢/1000 gallons for ammonia removal by zeolites. More reliable cost estimates will be available at the conclusion of present pilot plant studies. Alternative methods of regenerating zeolites which convert the ammonia to nitrogen gas are also being investigated.

The above paper was delivered at Dallas, Texas by J. B. Farrell. In order to make more information available than is presented in the paper, a number of the slides used in the oral presentation have been attached below.


Cation-Exchange Resin

Anion-Exchange Resin

R⁻ Na⁺
R⁻ Na⁺
R⁻ Na⁺
R⁻ Na⁺
+ 6NH₄⁺ →
R⁻ NH₄⁺
R⁻ NH₄⁺
R⁻ Na⁺
R⁻ Na⁺
+ 4NH₄⁺ + 2Na⁺
R⁺ Cl⁻
R⁺ Cl⁻
R⁺ Cl⁻
R⁺ Cl⁻
+ 6NO₃⁻ →
R⁺ NO₃⁻
R⁺ Cl⁻
R⁺ Cl⁻
R⁺ NO₃⁻
+ 4NO₃⁻ + 2Cl⁻

FIGURE 1

REMOVAL OF IONS FROM AQUEOUS SOLUTION

BY MEANS OF ION-EXCHANGE RESINS

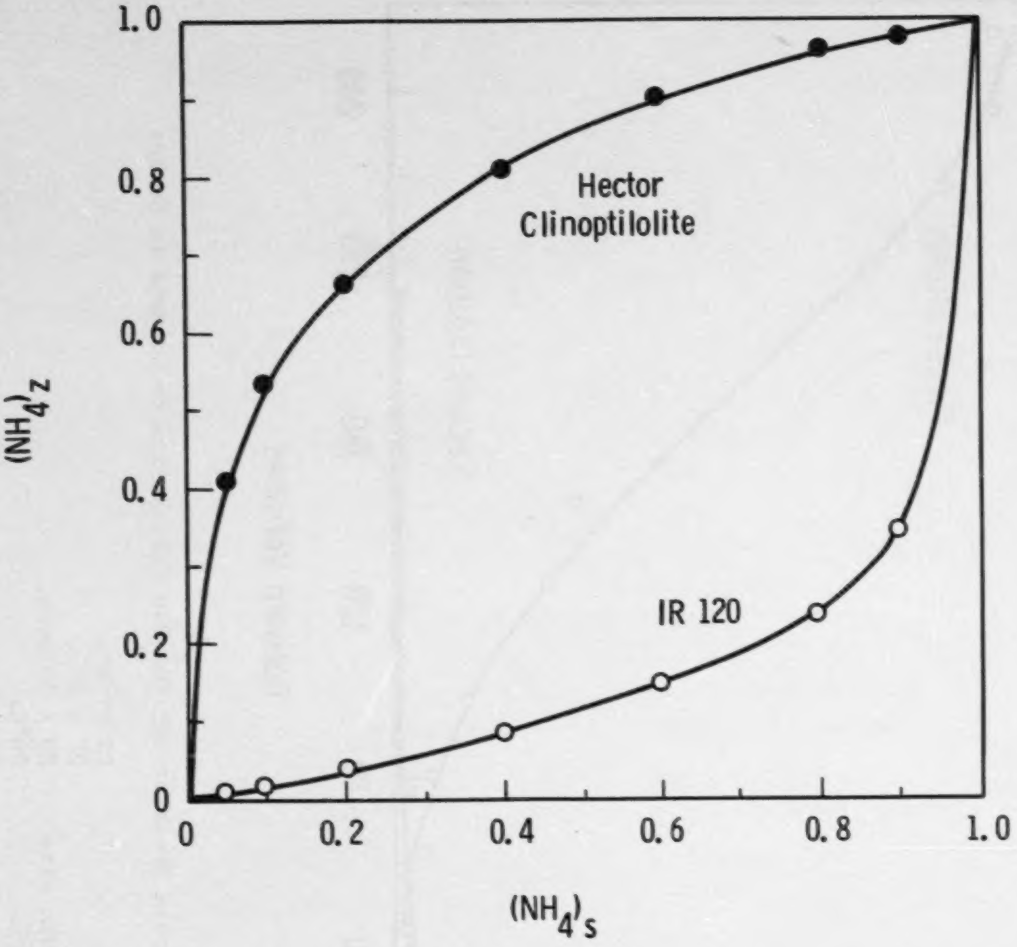


Figure 2. The 23°C isotherms for the reaction, $(Ca)_z + 2(NH_{4_N}) = 2(NH_4)_z + (Ca_N)$ with Hector clinoptilolite and IR 120. Total equilibrium solution normality was constant at $0.1\underline{N}(Ca)_z$, $(NH_4)_z$ = equivalent fraction of calcium or ammonium on the zeolite. (Ca_N), (NH_{4_N}) = normality of calcium or ammonium in the equilibrium solution. The ammonium capacity of IR 120 was 4.29 meq/g of air-dried resin.

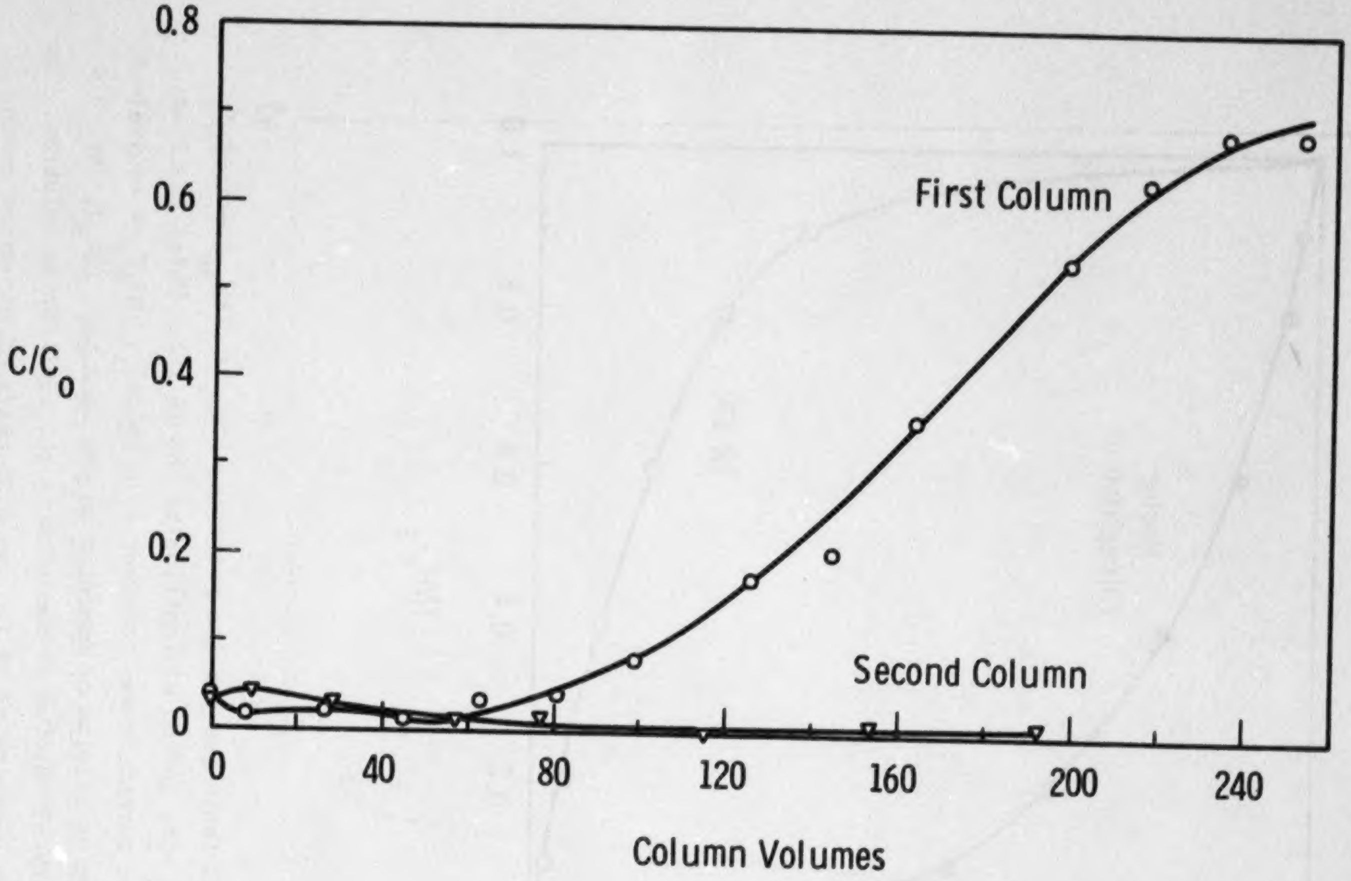


Figure 11. Ammonia Breakthrough for Two Clinoptilolite Columns in Series

Flow rate	20 cv/hr.
Column dimensions	2" x 24".
Clinoptilolite grain size	20 x 50 mesh.
Temperature	26°C.
Feed	Alum coagulated and filtered Richland Effluent NH_3 - N content 18.5 mg/l.
Previous regeneration	0.015N NaOH at 10 cv/hr, 40 cv total.

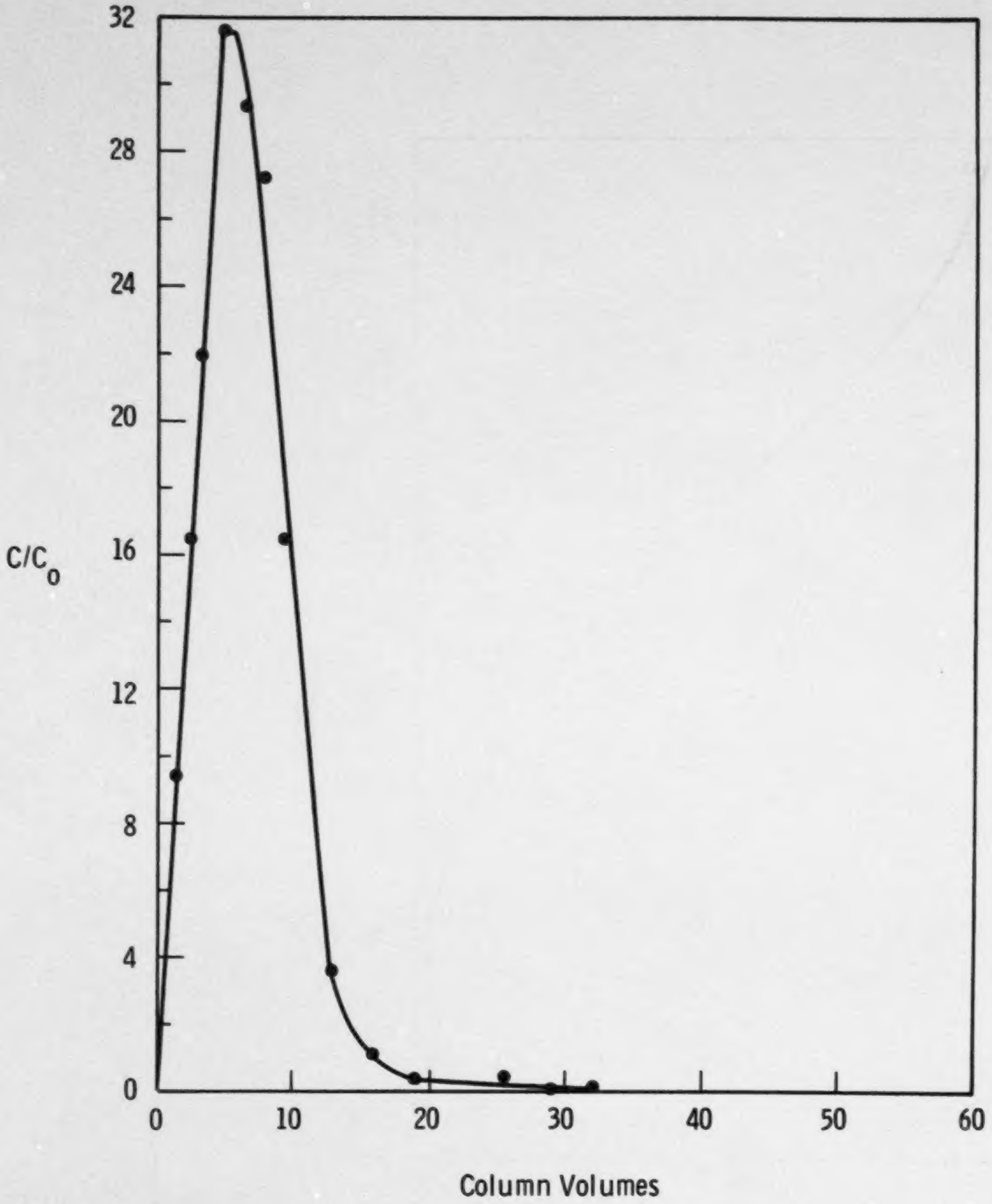


Figure 12. Ammonia Elution with Recycled Regenerant Saturated with Lime.

Flow rate	10 cv/hr upflow.
Column dimensions	2" x 24".
Clinoptilolite.	20 x 50 mesh.
Temperature	26°C.

Paper No. 6

ION EXCHANGE FOR NITRATE REMOVAL

R. A. Dobbs

Ion exchange is a standard unit process in the water treatment field. Large units have been installed for softening municipal water supplies. The resins used are fairly selective for the divalent cations of calcium and magnesium which are responsible for most of the hardness in water. Unfortunately, a comparable resin with a high selectivity for nitrate ion over other anions does not exist.

A technical and economic evaluation of the feasibility of removing nitrate from irrigation return drain water has been made by the Dow Chemical Company (1968). Although the concentration of anions in the drain water is considerably higher than the corresponding concentration in wastewater, the ratio of nitrate to chloride is quite similar for both waters. Several conclusions related to the drain water can be extrapolated to municipal wastewater. Commercially available anion exchange resins have a selectivity for nitrate over chloride. In order to develop an economic process this selectivity ratio should be approximately 20.

Even if resins of the required selectivity could be developed, additional problems must be solved in order to make the process practical. Regeneration of selective ion exchange resins are usually difficult. Based on the nitrate anion alone, efficiency of sodium chloride regeneration is of the order of 1%. Another serious problem involves the ultimate disposal of the nitrate laden brine produced during regeneration. Theoretically, resin regeneration could be achieved with sodium sulfate. Nitrate could be reduced chemically with ferrous sulfate and neutralized with lime to produce sludges and nitrogen gas as discussed in the next section. However, chemical and sludge disposal costs are likely to make the process uneconomical. In the brine regeneration process the high concentration (15%) of salt suggests the possibility of electrochemical treatment of the regenerant to produce nitrogen gas and chlorine.

Several attempts have been made to develop selective ion-exchange processes for nitrate removal. Dow Chemical Company is presently under contract (Contract No. 14-12-808) to develop a nitrate removal process based on the use of a porous solid absorbent containing a nitrate-selective water-immiscible extractant. The process has the advantages of liquid ion-exchange technology and the ease of operation of the granular bead resin systems.

Selective nitrate removal by ion exchange will not be feasible until new resins are synthesized with a high selectivity for nitrate over other anions present in the water. In addition, a suitable process for treating the nitrate laden regenerants must be developed.

Paper No. 7

OTHER METHODS FOR REMOVING NITROGEN

R. B. Dean

In addition to ammonia, nitrites and nitrates already discussed, nitrogen can occur in wastewaters in several other forms. Small concentrations of amino acids are leached from bacteria under anaerobic conditions. Digester supernatants contain a relatively high concentration of soluble amino acids and secondary clarifiers may release substantial quantities of amino acids if anaerobic conditions are approached in the return sludge. Amino acids are readily biodegraded and are removed in part by lime precipitation and carbon columns. Nitrilotriacetic acid (NTA) has been proposed as a detergent additive to chelate calcium ions as a partial replacement for phosphates. NTA is biodegraded in a well-operated secondary treatment plant. (Bunch and Ettinger, 1967) It is not removed by precipitation with aluminum hydroxide. The behavior of NTA toward precipitation by lime or iron salts and its behavior in the column of activated carbon containing adsorbed organic matter and a bacterial flora are now being studied at Cincinnati. NTA levels in wastewater are not expected to exceed about 2 mg/l as nitrogen.

Urea is the principal form in which nitrogen is excreted. Fortunately, urea is rapidly hydrolyzed to ammonia by bacteria in sewer lines and biological treatment plants. In the absence of biological action it would be extremely difficult to precipitate or adsorb urea from solution. Organic nitrogen is also present in particulate form both in raw sewage and in secondary effluents. In the latter case bacteria and bacterial fragments account for nearly all the suspended nitrogen. Efficient clarification and filtration are effective ways of removing this form of nitrogen. Typically, the organic nitrogen in the product from a carbon column following secondary treatment is approximately 1.0 mg N/l. This residue has not been characterized but it may be derived from bacterial action.

Soluble nitrogen compounds, with the exception of urea, are ionized in water and 85-90 percent of them can be removed by any deionizing or desalting process such as reverse osmosis, electrodialysis, ion exchange or distillation. None of these processes have a favorable selectivity for ammonium or nitrate ions and it is, therefore, necessary to remove about

90 percent of the salts in order to remove 90 percent of the soluble nitrogen compounds. Distillation is particularly unfavorable since it tends to concentrate ammonia in the distillate unless the feed is kept highly acidic. In that case, nitrous acid will be selectively distilled over (O'Connor et al., 1967). All of the general salt removal techniques are of interest only for water that is to be reused and are too expensive for consideration as treatments for wastes to be discharged to surface waters.

Chlorination of Ammonia. Ammonia reacts with chlorine stepwise according to the following equations:

(1) $Cl_2 + NH_3 \longrightarrow HCl + NH_2Cl$, monochloramine

(2) $Cl_2 + NH_2Cl \longrightarrow HCl + NHCl_2$, dichloramine

(3) $Cl_2 + NHCl_2 \longrightarrow HCl + NCl_3$, trichloramine

Monochloramine is rapidly decomposed to NH_3 and HCl by active carbon. The theoretical breakpoint equation is:

(4) $3\,Cl_2 + 2NH_3 \longrightarrow N_2 + 6HCl$

Actually 4 Cl_2 per $2NH_3$ or 10 mg of chlorine per mg of ammonia nitrogen is required. This means that some higher oxides of nitrogen must be produced in the reaction. A large number of possible compounds may be formed but unfortunately it is difficult to identify them analytically without very sophisticated procedures. Four moles of chlorine per mole of N_2 corresponds to 10 parts of chlorine for each part of ammonia nitrogen. The per capita excretion of ammonia nitrogen is of the order of 10 lbs. per year, equivalent to 100 lbs. of chlorine. A city of 200,000 would, therefore, require about 20 million lbs. or 10,000 tons of chlorine each year. Transport and handling of this amount of chlorine would be hazardous. Also, the use of chlorine would produce an equivalent weight of hydrochloric acid, which would exceed the buffer capacity of most waste waters, and would produce the highly odorous NCl_3. While hydrochloric acid would be effectively neutralized by discharge into the ocean and most surface waters, it could be a serious pollutant and discharge pipes would have to be made of special acid resistant materials. Sodium or calcium hypochlorite can be substituted for chlorine in equations (1-4).

$$(5)\quad 3NaOCl + 2NH_3 \longrightarrow N_2 + NaCl + 3H_2O$$

No excess hydrochloric acid is produced by the use of sodium hypochlorite, but again it will be necessary to use four moles of hypochlorite per mole of nitrogen or equivalent. Hypochlorite is more expensive than chlorine but is so much safer to use that New York City, Chicago, and other large cities have converted to aqueous hypochlorite for chlorination of water and treated wastes.

Chlorine is manufactured electrolytically according to equation (3):

$$(6)\quad 2NaCl + 2H_2O \longrightarrow H_2 + Cl_2 + 2NaOH$$

Sodium hypochlorite is made by the reaction of chlorine and NaOH. If this is done in the electrolytic cell, equation (4) results.

$$(7)\quad NaCl + H_2O \longrightarrow H_2 + NaOCl$$

Electrochemical production of chlorine or sodium hypochlorite has been practiced for sewage chlorination and treatment for years (Marson, 1967). It has never been optimized. Some source of brine is necessary to raise the conductivity of the water; therefore, electrochemical production of chlorine or hypochlorite has only been attractive for seacoast communities. Breakpoint chlorine treatment, of course, also disinfects as well as destroys ammonia. However, the addition of 200-300 mg/l of chloride might not be acceptable in inland waters.

Just as ammonia can be oxidized to nitrogen, so can nitrate be reduced to nitrogen. In acid media, nitrous acid derived from nitrites reacts with ammonia and amines to liberate nitrogen gas.

$$(8)\quad HNO_2 + RNH_2 \longrightarrow ROH + N_2 + H_2O$$

This reaction, called the Van Slyke reaction, does not proceed in neutral waters. (Brezonik and Lee, 1966) Chemical reduction of nitrates in dilute solution has been accomplished using ferrous sulfate to produce nitrogen gas and some nitrous oxide, N_2O. (Gunderloy et al., 1968) The by-product is a voluminous sludge of ferrous-ferric hydroxide. Some of the sulfate is incorporated in the precipitate but a large part of the sulfate remains in the waste. This process is being studied under contract and at present appears to have marginal value for special situations.

Costs of any of the processes discussed in this section are probably higher than costs for the more promising processes. The only cost that can be calculated direct with some confidence is the cost for chlorine to oxidize ammonia. Assuming 20 parts of ammonia nitrogen in a secondary effluent, 200 parts of chlorine would be required for breakpoint chlorination. This is equivalent to 1.5 lbs. of chlorine per 1000 gallons or about 6¢/1000 gal. To this must be added the cost of handling the corrosive hydrochloric acid produced. Sodium hypochlorite may cost twice as much as chlorine but associated costs are greatly reduced. The cost of electrically generated chlorine or hypochlorite will depend on the cost of electrodes and the possibility of using low-cost off-peak power.

SALT CREEK TWO STAGE NITRIFICATION PLANT
METROPOLITAN SANITARY DISTRICT OF GREATER CHICAGO

by

Richard L. Woodward, Associate
Camp, Dresser & McKee

The proposed Salt Creek Water Reclamation plant of the Metropolitan Sanitary District of Greater Chicago will serve an area of some 49 square miles in the northwestern part of Cook County about 20 to 25 miles northwest of downtown Chicago. It is primarily a residential area with some light industry. A portion of the area is served by combined sewers. At present, the area is tributary to the North Side or West-Southwest treatment plants but because of the rapid growth of this portion of metropolitan Chicago a decision was reached following a 1965 study by Greeley and Hansen to construct several treatment plants to serve the area rather than to build relief interceptors and to expand the existing plants.

Salt Creek is a tributary of the Des Plaines River. It rises in northwestern Cook County and flows across the northeastern part of Du Page County before reentering Cook County and joining the Des Plaines River. The outfall sewer from the Salt Creek treatment plant will discharge to Salt Creek a short distance above the Cook-Du Page county line and a short distance downstream from a proposed reservoir which is to be built in the Ned Brown Forest Preserve. During the summer months there will be virtually no dilution available for the effluent from the treatment plant. Through much of its length Salt Creek flows through park and forest preserve lands which are used for recreation by large numbers of people. Although the stream is not used to any appreciable extent for body contact recreation it is important that it be maintained as an attractive part of the landscape.

The Illinois Sanitary Water Board has established water quality standards and effluent standards which require an effluent of quite high quality from the Salt Creek plant. Some of the most pertinent of these are:

	Standards	Influent Wastewater
BOD	4 mg/l	95 mg/l
Suspended Solids	5 mg/l	188 mg/l
Ammonia Nitrogen	2.5 mg/l	20 mg/l
Nitrate Nitrogen	45 mg/l	--
Fecal Coliforms	2,000 per 100 ml	--

There is not at present any effluent or stream standard for phosphates in this area.

The wastewater to be treated at the Salt Creek plant is comparatively dilute. A sampling program of one week's duration of the principal sewer which will be tributary to the plant showed the average characteristics summarized in the table.

Treatment Processes Considered

The high effluent quality demanded requires that the treatment process remove most of the carbonaceous and nitrogenous oxygen demanding materials. The two principal processes which had been developed at the time of our studies (late 1967) for removing ammonia were air stripping, which had been studied at Lake Tahoe and nitrification which had been studied by a great many investigators.

Ammonia stripping was considered but was found to be more costly and less reliable than nitrification. The high alkalinity and hardness of this wastewater would have required very large quantities of lime and produced correspondingly large quantities of sludge to be processed. At the low temperatures which prevail in the Chicago area in the winter the process would be quite inefficient in ammonia removal and would probably have to be discontinued because of icing and other operating difficulties.

The nitrification process in activated sludge systems is fairly well understood now as a result of the work of a number of investigators both here and abroad. Downing and his colleagues at the Water Pollution Research Laboratory in England have contributed most significantly to this understanding. The basic requirement for maintaining a nitrifying flora in an activated sludge system is that the overall rate of sludge growth (and hence of sludge wasting) be no greater than the rate of growth of the nitrifying organisms. In a conventional system this requires relatively long cell residence times in order that much of the sludge produced as a result of the activity of the heterotrophs in removing carbonaceous material will be aerobically digested. However, for one reason or another, many plants which provide long cell residence times appear to be rather erratic in nitrifying. Just why this is so remains puzzling.

Barth and his colleagues at the Robert A. Taft Sanitary Engineering Center have worked with a two-stage activated sludge system which appeared to offer a number of advantages over the conventional one-stage systems where reliable nitrification is called for. In this system, the first aeration stage is devoted to removal of most of the carbonaceous material and the second stage largely to nitrification. By maintaining these two separate specialized sludges it is possible to achieve such long residence times in the second stage that nitrification will proceed even at relatively low temperatures without providing as long aeration times as would be needed in a conventional system.

After some comparative cost studies this two-stage system was recommended to the Sanitary District and was approved by them. To achieve the very low suspended solids and BOD concentrations called for, filters were provided following the second-stage clarifiers. Chlorination will be provided either before or after the filters to meet the coliform standard of the Illinois Sanitary Water Board.

Nutrient Removal

At present, the prescribed water quality standards do not require removal of either nitrogen or phosphorus, but this type of plant has the capability of providing for nutrient removal without appreciable additional capital cost. Such provisions have been made in the design of the plant.

Phosphate removal can be accomplished by adding an iron or aluminum salt to the first aeration stage. This has been studied by Barth and his colleagues as well as by a number of other investigators. At the Salt Creek plant provision has been made for such chemical additions.

Nitrogen removal by denitrification can be accomplished in the filters which follow the second-stage clarifiers by providing a carbon source to permit the development of a denitrifying flora in the filters. This process has been investigated at Pomona, California by the Federal Water Quality Administration and the Los Angeles County Sanitation District. Provisions for feeding methanol as a carbon source are included in the Salt Creek design.

It is not known to what extent nutrient removal will be practiced at Salt Creek, but it was relatively inexpensive to provide such capability.

Pilot Plant Studies

The Sanitary District was anxious to proceed immediately to final design of the Salt Creek plant after approval of our report in early 1968. The deadline for completion of final plans and specifications was December, 1969. Provisions were made to convert a one million gallon per day sewage treatment plant which the District operates at Hazelcrest, Illinois in southern Cook County to the type of process contemplated for Salt Creek. This was done and the plant was operated during part of 1969. It was not possible to develop a nitrifying flora until the sewage temperature reached about 60° F, but thereafter the plant operated smoothly with almost complete nitrification even after cold weather had reduced sewage temperatures to the 40's.

The nutrient removal facilities of the plant were tested to only a limited extent. No problems were experienced with phosphate removal by feeding sodium aluminate. The denitrification step encountered difficulties which were related more to equipment provided in the pilot plant than to the process. These should not be a problem in the full scale plants.

Plant Design

The design calls for the plant to handle an average flow of 30 mgd during dry weather with 50 mgd on maximum dry weather days. During wet weather 50 mgd will be given complete treatment. Wet weather flows above 50 mgd will receive sedimentation and chlorination. After coarse racks, pumping, screening and grit removal the sewage will flow to the first aeration stage which will provide three hours detention at 50 mgd. Sedimentation will be in circular clarifiers with an overflow rate of 1,450 gallons per day per square foot based on maximum day flow plus 30 percent sludge return. The second-stage clarifiers and sedimentation tanks will be the same as the first stage. Filters will have three feet of anthracite and sand media and will be designed to operate at six gallons per minute per square foot.

Sludge will be thickened in air flotation thickeners, digested and pumped to a land reclamation site. The Salt Creek plant will provide digestion facilities for sludge from another plant to be built in this part of the Sanitary District.

Chemical feeding facilities will permit feeding alum to the first aeration stage and also to the influent to the filters. Polyelectrolytes can also be fed as filter aids to the filter influent and to assist in sludge thickening. Methanol can be added to the filter influent if denitrification is desired. Chlorine can be added at a number of points in the system to deal with odor problems or to disinfect.

The plant is designed as the first stage of construction to be expanded ultimately to three times its initial size.

BIBLIOGRAPHY

AWWA Committee Report, 1970. "Chemistry of Nitrogen and Phosphorus in Water," 62(2), 127-140.

Barth, E. F., et al., 1968. "Chemical-Biological Control of Nitrogen and Phosphorus in Wastewater Effluent," J. Water Pol. Control Fed., Vol. 40, 2040.

Bartsch, A. F., 1970. Personal communication.

Battelle Memorial Institute, Pacific Northwest Laboratories, March 1969. "Ammonia Removal from Agricultural Runoff and Secondary Effluents by Selected Ion Exchange," U.S. Dept. of Interior, FWPCA, Report TWRC-5.

Brezonik, P. T., and Lee, G. F., 1966. "Sources of Elemental Nitrogen in Fermentation Gases," Air & Wat. Pol. Int. J., Pergamon Press, 10, 145-160.

Bringmann, G., and Kuhn, R., 1965. "Schnell-denitrifikation im underdruck-verfahren," Gesundheits-Ingenieur, Vol. 86, 16.

Bunch, R. L., and Ettinger, M. B., 1967. "Biodegradability of Potential Organic Substitutes for Phosphates," 22nd Annual Purdue Industrial Waste Conference, Purdue University, Lafayette, Ind., 393-396.

Carey, C., Sept. 1968. "Column Denitrification at Pomona, California," 41st Annual Conference Water Pollution Control Federation, Chicago, Illinois.

Dow Chemical Company, August 26, 1968. "Feasibility of Removal of Nitrates from San Luis Drain Waters by Ion Exchange," Final Report Contract No. 14-06-D-6434, U.S. Bureau of Reclamation, Department of Interior.

Downing, A. L., and Hopwood, A. P., 1964. "Some Observations on the Kinetics of Nitrifying Activated-Sludge Plants," Schweizerische Zeitschrift fur Hydrologie, Vol. XXVI, Fasc. 2, 271-288.

Echelberger, W. F., and Tenney, M. W., 1969. "Control of Organic and Eutrophying Pollutants by Combined Chemical and Biological Wastewater Treatment," Division of Water, Air and Waste Chemistry, American Chemical Society, Minneapolis, Minnesota.

Flaigg, N. G., and Reid, G. W., 1954. "Effects of Nitrogenous Compounds on Stream Conditions," Sewage Ind. Wastes, 26(9), 1145-54.

Gunderloy, F. C. Jr., et al., Oct. 1968. "Dilute Solution Reactions of the Nitrate Ion as Applied to Water Reclamation," U.S. Dept. of Interior, FWPCA, Report TWRC-1.

Jaworski, N., 1970. Personal communication.

Jenkins, S. H., 1970. "British Water Pollution Control," Environmental Science & Technology, 4(3), 204-209.

Kuhn, P. A., 1956. "Removal of Ammonium Nitrogen from Sewage Effluent," M.S. Thesis, University of Wisconsin.

Lang, M., 1966. "Chemical Control of Water Quality in a Tidal Basin," J. Water Pol. Control Fed., 38(9) 1410-18.

Marson, H. W., 1967. "Electrolytic Methods in Modern Sewage Treatment," Effl. Wat Treat. J., 7, 71-73 and 75-77.

McCarty, P. L., Beck, L., and St. Amant, P., May 6, 1969. "Biological Denitrification of Wastewaters by Addition of Organic Materials," 24th Annual Purdue Industrial Waste Conference, Purdue University, Lafayette, Indiana.

McKee, J. E., and Wolf, H. W., 1963. "Water Quality Criteria," 2nd Ed. Publication 3A, California State Water Quality Control Board, Sacramento, Calif., 134.

Mercer, B. W., Ames, L. L. Jr., Touhill, C. J., Van Slyke, W. J., and Dean, R. B., 1970. "Ammonia Removal from Secondary Effluents by Selective Ion Exchange," J. Water Pol. Control Fed., 42, R 95-107.

Miner, S, 1969. "Preliminary Air Pollution Survey of Ammonia." PHS National Air Pollution Control Administration Publication No. APTD 69-25. (Work done under Contract No. PH 22-68-25 with Litton Systems, Inc.)

Mulbarger, M. C., et al., April 1969. "Manassas, Va., Adds Nutrient Removal to Waste Treatment," Water and Wastes Engineering, 46.

O'Connor, B., et al., 1967. "Laboratory Distillation of Municipal Waste Effluents," J. Water Pol. Control Fed., 39(10 part 2), R 25-31.

Osborn, D. W., 1965. "Operating Experiences with Double Filtration in Johannesburg," J. of the Institute of Sewage Purification, Part 3, 272.

PAAP, Feb. 1969. "Provisional Algal Assay Procedure," Joint Industry, Government Task Force on Eutrophication, P.O. Box 3011, Grand Central Station, New York, N.Y., 10017.

Roesler, J. F., Smith, R., and Eilers, R. G., 1970. "Mathematical Similation of Ammonia Stripping Towers for Wastewater Treatment," Internal Report, Advanced Waste Treatment Research Laboratory, Cincinnati, Ohio.

Sawyer, C., February 18, 1970. Personal communication.

Slechta, A. F., and Culp, G. L., 1967. "Water Reclamation Studies at the South Tahoe Public Utility District," J. Wat. Poll. Control Fed., 39(5), 787-813.

Smith, John M., May 1969 to March 1970. Data from experimental results contained in monthly report. Research concluded at Lebanon, Ohio, pilot plant by John M. Smith.

St. Amant, P. P. and McCarty, P. L., 1969. "Treatment of High Nitrate Waters," JAWWA, 61 (12), 659-662.

Suhr, L. G., 1969. "Nutrient Removal at Lake Tahoe, Costs and Criteria," communicated to R. B. Dean.

Tamblyn, T. A., and Sword, B. R., 1969. "The Aerobic Filter for the Denitrification of Agricultural Subsurface Drainage," 24th Purdue Industrial Waste Conference.

van Schreven, D. A., 1963. "Nitrogen Transformations in the Former Subaqueous Soils of Polders Recently Reclaimed from Lake Ijssel. Losses of Nitrogen Due to Denitrification and Leaching." International J. of Plant Nutrition, Plant Chemistry, Soil Microbiology and Soil-borne Plant Diseases, Vol. 17, 163.

van Vuuren, L. R., January 21, 1970. Personal communication to R. Culp.

Wuhrman, K., 1960. "Effect of Oxygen Tension on Biochemical Reactions in Biological Treatment Plants," Paper No. 3, Conference on Biological Waste Treatment, Manhattan College, New York.